STATUS OF INSECTICIDE RESIDUES AND IMPACT OF INTEGRATED PEST MANAGEMENT

BY

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CERTIFICATE

Ms. **B. RATNA KUMARI** has satisfactorily prosecuted the course of research and that the thesis entitled **"Status of Insecticide Residues and Impact of Integrated Pest Management"** submitted is the result of original research work and is of sufficiently high standard to warrant its presentation to the examination. I also certify that the thesis or part thereof has not been previously submitted by her for a degree of any university.

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This is to certify that the thesis entitled **"Status of Insecticide Residues and Impact of Integrated Pest Management"** submitted in partial fulfillment of the requirements for the degree of **DOCTOR OF PHILOSOPHY in Agriculture** of the Acharya N G Ranga Agricultural University is a record of the bonafide research work carried out by Ms. **B. RATNA KUMARI** under our guidance and supervision. The subject of the thesis has been approved by the Student's Advisory Committee.

No part of the thesis has been submitted by the student for any other degree or diploma. The published part has been fully acknowledged. All the assistance and help received during the course of investigation has been acknowledged by the author of the thesis.

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Date: 06-10-2010 **(B. RATNA KUMARI)**

DECLARATION

I, **B. RATNA KUMARI,** here by declare that the thesis entitled **"Status of Insecticide Residues and Impact of Integrated Pest Management"** submitted to Acharya N G Ranga Agricultural University for the degree of **DOCTOR OF PHILOSOPHY in Agriculture** is a result of original research work done by me. I also declare that the material contained in this thesis or part thereof has not been published earlier in any manner.

Date: 06-10-2010

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LIST OF SYMBOLS, ABBREVIATIONS, AND ACRONYMS

%	:	per cent
$		Dollar
@	:	at the rate of
<	:	less than
≤	:	less than or equal to
>	:	greater than
^0C	:	degrees centigrade
a.i	:	Active ingredient
ADI	:	Acceptable Daily Intake
ADW		Agricultural drainage water
AF	:	Aerosol formulation
AICRP		All India coordinated research project
AINP-PR		All India network project on pesticide residues
AOAC		Association of official analytical chemists methods
BHC		Benzene hexa chloride
BPMC	:	O-sec-butyl phenyl N-methyl carbamate
CFRL		Central Food Research Laboratory
cm	:	Centimeter
DAT	:	Days after treatment
DDD	:	Dichloro diphenyl dichloroethane
DDT		Dichlorodiphenyltrichloroethane
DDVP	:	Dimethyl dichlorovinyl phosphate
EC	:	Emulsifiable concentrate
EEP		Environment exposure to pesticides
et al.	:	and others
FAO	:	Food and Agricultural Organization
Fig.	:	Figure
G	:	Gram
g	:	Gram
g ha^{-1}	:	Gram per hectare
g L^{-1}	:	Gram per liter
GAP		Good agricultural practices
GC-ECD	:	Gas chromatography-electron capture detector
GC-FID	:	Gas chromatography-Flame ionization detector
GC-MS		Gas chromatography-Mass spectrometer
GC-NPD	:	Gas chromatography-Nitrogen phosphorus detector
GLC		Gas liquid chromatography
GW		Ground water

H	:	Hour
Ha	:	Hectare
HaNPV	:	*Helicoverpa armigera* Nuclear Polyhedrosis Virus
HCH		Hexa chloro cyclohexane
HPLC	:	High Performance Liquid Chromatography
HPTLC		High performance thin layer chromatography
i.e	:	That is
ICAR	:	Indian council of agricultural research
ICRISAT	:	International Crops Research Institute for Semi Arid Tropics
IPM		Integrated Pest Management
Kg	:	Kilogram
Kg ha^{-1}	:	Kilograms per hectare
L	:	Litre
l ha^{-1}	:	Litres per hectare
LE ha^{-1}	:	Larval equivalents per hectare
LOD	:	Limit of Detection
LOQ	:	Limit of Quantification
M	:	Meter
MAC		Maximum Acceptable Concentration
Mg	:	Milligram
mg g^{-1}	:	Milligrams per gram
mg kg^{-1}	:	Milligram per kilogram
mg ml^{-1}	:	Milligrams per milliliter
Min	:	Minute
ml	:	Milliliter
ml ha^{-1}	:	Milliliters per hectare
ml min^{-1}	:	Milliliters per minute
ml^{-1}	:	Per milliliter
mm	:	Millimeter
MRL		Maximum Residue Limit
MRMs		Multiresidue methods
mT	:	Metric tons
mv	:	Milli volts
NaCl	:	Sodium Chloride
NaOH	:	Sodium Hydroxide
ND	:	Not detectable
NDR		No detectable residues
ng	:	Nanogram
ng g^{-1}	:	Nanograms per gram
ng L^{-1}	:	Nanogram per liter

ng ml^{-1}	:	Nanograms per milliliter
NIOH	:	National institute for occupational health
Non-IPM		Non Integrated Pest Management
NSKE		Neem Seed Kernal Extract
NW		Nile water
p, p'-DDE	:	Para para dichloro diphenyl ethane
p, p'-TDE	:	Para para tetrachloro diphenyl ethane
pH	:	Negative logarithm of Hydrogen ion (-log [H^+])
POP		Persistent organic pollutant
ppb	:	Parts per billion
ppm	:	Parts per million
q ha^{-1}	:	quintals per hectare
rpm	:	Rotations per minute
RSD		Relative standard deviation
RT	:	Retention time
SD	:	Standard deviation
SIM	:	Selective Ion Monitoring
SIM		Selected ion monitoring
SP	:	Soluble powder
SPE		Solid phase extraction
SW		Sewage water
Tr	:	Traces
UNEP		United nations environmental programme
US	:	United States
viz.,	:	Namely
WG	:	Wettable granules
WHO	:	World Health Organisation
WP	:	Wettable powder
WSC	:	Water soluble concentrate
α	:	Alpha
β	:	Beta
δ	:	Delta
µg	:	Microgram
µg kg^{-1}	:	Microgram per kilogram
µg ml^{-1}	:	micrograms per milliliter
µg µl^{-1}	:	micrograms per microliter
µl	:	Microliter

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ABSTRACT

The present research was taken up to study the **"Status of insecticide residues and impact of Integrated Pest Management (IPM)".** The field studies were conducted to monitor the insecticide residues on food crops (rice, maize, pigeonpea), cotton, vegetables, soil and water and to know the impact of Integrated Pest Management (IPM) in reducing insecticide residues. The laboratory experiments were conducted in Pesticide Residue Laboratory at the International Crops Research Institute for the Semi-Arid Tropics (ICRISAT), Patancheru, India. Participatory rural appraisal (PRA) was undertaken in Kothapally watershed (IPM village) and Enkepally (non-IPM village).

Among the food crops and cotton analysed for presence of insecticide residues (monocrotophos, chlorpyriphos, alpha endosulfan, beta endosulfan and cypermethrin), one rice grain sample (0.5 $\mu g\ g^{-1}$) out of 5 samples collected from Kothapally was contaminated and among the soil samples, residues were detected in one soil sample (0.02 $\mu g\ g^{-1}$) collected from maize field during 2008 in Enkepally. Only two samples were contaminated -- one rice grain sample (0.008 $\mu g\ g^{-1}$) and one soil sample (0.03 $\mu g\ g^{-1}$) collected from rice field during 2009 from Enkepally.

Out of the total 45 tomato fruit samples from Kothapally analysed for insecticide residues over a period of five seasons in 2008 and 2009, 11 samples (24%) were found to contain residues. In Enkepally, the residues were observed in 50% of samples (15 out of 30 samples) during this period. However, none of the samples from Kothapally and 7% of contaminated samples from Enkepally had residues above MRLs.

Overall, out of the 30 soil samples collected from tomato fields during 2008 and 2009, only six samples (20%) contained insecticide residues. Out of the 20 soil samples drawn from Enkepally, 7 (35%) were contaminated.

Among the 40 brinjal samples analysed during 2008 and 2009 seasons, 17 (43%) samples from Kothapally and 29 (73%) samples from the Enkepally contained insecticide residues. The overall residue levels in brinjal during the study period indicated 7% of samples in Enkepally above MRLs.

Soil analysis in five various seasons showed that only 10% and 15% of the samples collected from brinjal fields were contaminated in Kothapally and Enkepally, respectively and none of the water samples collected from food crops, cotton and vegetable crops were contaminated.

Participatory rural appraisal brought out that most of the farmers (80-86%) initiate the plant protection practices based on the first appearance of the pest in both the villages irrespective of pest population, crop stage and the damage caused.

Thirty eight per cent of the farmers in Kothapally and 50% in Enkepally got their plant protection advice from pesticide dealers and on the other hand, 35% in Kothapally and 20% of the farmers in Enkepally adopted plant protection advice from the agricultural officers. Majority of farmers from Kothapally (40%) and Enkepally (32%) indicated that the poor efficacy of pesticides was due to the spurious pesticides in the market.

Only 32% of the farmers in Kothapally and 12% in the Enkepally used protective clothing while applying the toxic plant protection chemicals. Amongst the various health problems, farmers complained headache as the major health problem followed by skin rash and eye irritation.

Forty four per cent of the farmers in Kothapally and only 16% in Enkepally were aware of the residual effects of pesticides. Though the farmers were aware of a waiting period in reducing residues, only 30% of them were following the concept for a period of 2-5 days.

Although 48% of farmers in Kothapally and 16% in Enkepally were aware of IPM, only half of the farmers in Kothapally adopted it. Traditionally cotton was found to be heavily sprayed crop with 20-21 sprays, followed by vegetables (2-20). Among the vegetables, okra received more insecticide sprays (13, 20), followed by brinjal (12, 15), tomato (7, 9), cabbage (4, 8) and leafy vegetables (2, 8). Among the insecticides used, popular molecules like monocrotophos, endosulfan, cypermethrin, and fenvelarate dominated the plant protection scenario in both the villages.

Out of the 15 tomato fruit samples analysed for insecticide residues from IPM fields, only 3 samples (20% contamination) were found to contain residues compared to 47% in Non-IPM fields. Two soil samples out of the 10 samples from non-IPM tomato fields analysed were found to contain residues.

In brinjal, 20% of the samples under IPM treatment and 47% in non-IPM had contamination. Twenty per cent of soils in non-IPM fields had residues while none of the soil samples in IPM fields had residues. Water sample collected either from IPM (or) non-IPM vegetable fields contained no residues above the detectable level. Though the contamination levels in crops and soils in IPM and non-IPM fields indicated substantial differences, the residue concentrations were below MRLs.

The GC-MS response for all analytes was linear in the concentration range of 0.05-1.0 $\mu g\ ml^{-1}$ assayed with correlation coefficients of >0.998. The reproducibility of the results for all the analytes ranged from 76.6% to 117.92% with low (<10%) relative standard deviation for all the matrices which are acceptable levels.

Thus the study defined the occurrence of insecticide residues in different crops and natural resources related to IPM and non-IPM situations.

INTRODUCTION

CHAPTER I

INTRODUCTION

Agricultural chemicals are used to improve the productivity and quality of produce and slow down the rate of deterioration. There is no point in producing food that is unsafe or will not last long enough to utilize. Like medicines prescribed by doctors, chemicals are used only if their benefits (in food production and storage) outweigh the risks to the people and livestock from their residues. Agricultural chemicals help countries to economically and efficiently feed their people and livestock. It is estimated globally that pests account for more than 40 per cent of the pre-harvest crop losses despite the use of chemicals. Of these losses, 15% are attributable to insects and 13% each to weeds and pathogens. An additional 10% is lost during post-harvest processing of the crop (Anonymous, 2007).

For enhancing productivity, the ecological principle is ignored by the cultivators that the poison introduced in the environment comes back through air, water and food because agriculture and the environment are intricately linked. The use of synthetic pesticides in Indian agriculture cannot be dispensed with for meeting the food, feed and fodder requirements of the increasing population. The eco-friendly agriculture with minimum dependence on the synthetic pesticides has been demonstrated successfully in selected isolated cases in the country. To be effective, agricultural chemicals must stay in place long enough to do their job. Persistence of toxic pesticide residues on fruits and vegetables when consumed fresh, may create health hazards to the consumers due to their toxic residues. Contact with clothes made from plant fibres containing DDT (Dichloro diphenyl

trichloroethane) residues can cause problems to the skin. During the Somaza regime in Nicargua, heavy applications of DDT on cotton resulted in the contamination of human breast milk in the urban areas. The chemical was found in mother's milk at levels 42-45 times above the World Health Organisation's (WHO) safe level (Anon, 1996). Studies from Anupgarh, Rajasthan, where intensive agriculture was taken up and farmers used high amounts of pesticides to boost crop productivity, exposure of humans to these hazardous chemicals directly in the fields and indirectly through contaminated diet resulted in the occurrence of organochlorine residues in blood (3.3-6.3 mg l^{-1}) and milk (3.2-4.6 mg l^{-1}) samples of the lactating women (Kumar *et al.*, 2005). High levels of pesticide residues (15-605 times) were observed in blood samples of cotton farmers from four villages of Punjab (Anon, 2005).

According to pesticide action network Asia Pacific, 1999 about 51% of food material is contaminated with residues in the developing world compared to 21% worldwide, of which 20% were above maximum residue limit (MRL) prescribed by Food and Agriculture Organisation (FAO) standards (Anon, 1999). In other words, 20% of this food is unfit for human consumption and still being consumed in the developing countries. The indiscriminate use of pesticides has increased mortality and morbidity of humans in the developing countries (Wilson and Tisdell, 2001). The World Health Organisation and the United Nations Environment Programme (UNEP) estimated that each year 3 million farm workers in the developing world experienced severe pesticide poisoning in which about 18000 were fatal (Miller, 2004). An excessive dependence on the chemical pesticides also leads to the development of resistance in insect pests to insecticides (Kranthi *et al.*, 2002).

Worldwide, approximately 80,000 chemicals have been introduced into the environment over the last 50 years, but virtually none have been tested for the full range of health effects particularly with reference to the persistence and residues in various environments. Pesticide use has increased rapidly over the last two decades at the rate of 12% per year (Thacker *et al.*, 2005). The total amount of pesticides used in India increased from 154 t in 1953-54 to nearly more than 84,000 t in 1993-94, and thereafter declined to 37,959 t by 2006-07 (Chandrasekaran *et al.*, 2008).

Approximately 2.5 million t of pesticides are consumed annually throughout the World. The UNEP estimated that accidental pesticide poisoning causes 20,000 deaths and 1 million cases of illness per year Worldwide (Meena *et al.*, 2008).

In the past few decades with the benefits of pesticides being clearly recognized, usage has steadily increased from 2.2 g ha^{-1} active ingredient (a.i.) in 1950 (Vasanthraj David, 1995) to the level of 381 g ha^{-1} by 2007 in India (which is about 170 fold) (Anon, 2009). Insecticide poisoning in agricultural workers is more pronounced as the safety precautions in handling and spraying remain grossly inadequate (Anon., 1999). However, considering the intensity of insecticide use in crops such as cotton and vegetables in India the insecticidal pressure on unit area is several folds higher than the global average insecticide use.

Literature survey shows that most of the studies on pesticides taken up in India reflect the presence of pesticide residues in significant amounts in food and agricultural commodities and pesticide pollution does exist in the country, and is a cause of concern for Public health. The presence of pesticide residues particularly persistent organochlorine insecticides in the environment and food

commodities is a matter of concern through out the Country (Kalra and Chawla 1985; Kanan *et al.*, 1992; Kumari and Kathpal 1995; Kumari *et al.*, 1996; 2002, 2003a; 2004; 2005; 2006).

Studies on the dietary intake of pesticide residues have been carried out in various parts of the world by several researchers (Kaphalia *et al.*, 1985; Tanabe *et al.*, 1991; Shukla *et al.*, 2002; Madan and Kathpal 2004). Earlier surveys made in India, showed high amount of pesticide residues in food commodities, mainly of organochlorine insecticides (Agnihotri *et al.*, 1974; Lakshminarayana and Menon, 1975; Kathpal, 1980; Khandekar *et al.*, 1982; Lal *et al.*, 1989).

Vegetables are an essential component of the human diet. Mostly, vegetable crops are cultivated under intensive plant protection for achieving higher production. This involves repeated application of pesticides for the control of various insect-pests but their indiscriminate use may create health hazards due to toxic residues that may persist in amounts above prescribed MRLs. The problem becomes more acute if the xenobiotics are used close to the harvest of the crop and during the transit. Hence, it becomes imperative to regularly monitor the vegetables for pesticide residues. In India, about 13-14% of the total pesticides used in agriculture are used for fruits and vegetables covering only 3% of total cropped area (Arora and Singh, 2004). Repeated application of pesticides on vegetable often results in the build up of their residues (Handa, 1992). Surveys carried out in the country indicate that 50-70% of vegetables are contaminated with insecticide residues (Karanth, 2000).

Several studies indicated the occurrence of pesticide residues in the farmgate or market samples of vegetables in India (Dethe *et al.*, 1995; Madan *et al.*, 1996; Awasthi and Ahuja 1997; Parihar *et al.*, 1997; Gupta *et al.*, 1998;

Singh *et al.*, 1999; ICAR, 2002; Arora and Gopal, 2002; Kumari *et al.*, 2003; 2004, 2005; Shashi *et al.*, 2005; Mayank and Ajay, 2005). On the other hand, studies on farmgate monitoring of vegetables carried out in different parts of India (Madan *et al.*, 1996; Chahal *et al.*, 1997; Parihar *et al.*, 1997; Gupta *et al.*, 1998; Singh *et al.*, 1999) revealed contamination mostly with organophosphorous and synthetic pyrethroid insecticides, indicating clearly the changes in the usage pattern from organochlorine to other groups of pesticides.

In general, about 50% of the chemical pesticides that are applied to the crops directly go into the soil and other non-targets. The chemical residues in the soil find their way to the aquatic systems or get accumulated in the plant products (grain, root. stem etc). Pesticides use or misuse may lead to serious ground water contamination. Pesticides enter the soil and ground water by direct treatment or get washed off from the plant surfaces during rainfall. Depending on the phenotype and density of the plant type, it is estimated that an average of 35-50% of the plant protection material is deposited on the soil immediately after spraying. The behavior of pesticides in soil and ground water involves persistence, movement and metabolism. The formation of residues in the soil mainly depends on water solubility and the binding capacity of both organic and inorganic constituents of the soil. Numerous studies over the past four decades have indicated that the downward and subsequent subsurface transport of pesticides applied at the land surface in agricultural areas can contribute to the contamination of ground water by these chemicals and their metabolites (Gilliom *et al.*, 2006; McMahon *et al.*, 2006). However, several cases of pesticide contamination of food, feed, fodder and water are not reported since people were not aware of the consequences of these

pollutants. It is therefore highly important to monitor surface, ground and drinking water for pesticide residues.

International buyers are more quality conscious and are reluctant to buy produce with quality constraints. The major hurdles in the Asian exports are aflatoxin and pesticide residues. The non-availability of MRLs for all the registered pesticides on all important (or) key crops is a major requirement in the absence of International MRLs to meet the challenges. The regular monitoring of various raw and processed food commodities help to contain the pesticide residue by promoting good agricultural practices (GAPs) with proper safe waiting period (Sreenivasa Rao *et al.*, 2005).

The MRL is the highest concentration of the residue allowed in food crops or animal products at harvest or sale, and is legally enforceable. Residues of an agricultural compound in food must be no higher than the MRL for that chemical. A residue found at or below the MRL indicates that the farmer or grower has met the requirements and used the compound properly. This is sometimes referred to as following 'good agricultural practice (GAP)'. The MRLs are set to ensure that at harvest or slaughter, the chemical will have done its job and the resulting residue is as low as possible. The MRL also takes into account any other relevant breakdown or metabolism of the chemicals in the plant or animal, as well as the residue of the agricultural compound itself. Even in the unlikely event if the food was bought with pesticide contamination above the MRL, the normal processes of storage (reduction over time), washing and cooking the food will, in most cases, significantly reduce the levels of residues for the majority of compounds.

Residue monitoring is directed towards enforcing the law to seize those samples that contain residues above tolerance limits and provides a check that farmers are complying with the instructions given on pesticide container label as in such case residues in crop should remain within acceptable limits. The determination of pesticide residues in food has become an increasingly essential requirement for the consumers, producers and authorities responsible for food quality control. Dietary intake of pesticides through contaminated food is the most predominant source of pesticide exposure in the general population.

For maintaining the quality of a commodity, it is essential to keep the produce free from any pesticide residues. A zero level residue in the finished product is not only desired but is also needed for eco-preservation and human health. Hence, it is time to promote safer and alternative practices to support the reduction in the use of toxic pesticides through the existing IPM (Integrated Pest Management) programs. The necessity of pesticide residue analysis in various agro-based commodities has become more relevant in the present context.

IPM is the most environment-friendly approach of crop-protection and prescribes the use of chemical pesticides as the last resort. However, most of the farming communities in India are not much educated. Therefore, they are averse to adopt the programme. Implementation of the IPM strategies reduces toxic pesticides in agriculture to enhance productivity of healthy products and profitability. The inclusion of eco-friendly IPM packages in the plant protection measures is the need of the hour to save the crop losses from the biotic stresses and to sustain and improve the agricultural production, soil health and the environment. The safety of agricultural chemicals used worldwide must be tested both locally

and internationally and then only they should be approved for use if they pose no greater risk to the consumers than the foods grown without their use.

In view of these problems, this study was undertaken with the following objectives:

1. To monitor the insecticide residues in different crops, soil and water in Kothapally watershed of RangaReddy district, Andhra Pradesh in the semi-arid region of India under farmer's insect pest management practices.
2. To evaluate the impact of IPM in reducing insecticide residues.

REVIEW OF LITERATURE

CHAPTER II

REVIEW OF LITERATURE

The hazards of toxic residues can be considerably reduced if the pesticides are used in accordance with "good agricultural practice" (GAP). The information on the levels of pesticide residues occurring in food commodities is essential and can be obtained through regular monitoring procedures. The literature pertaining to the monitoring of insecticide residues in food, feed and other commodities and the impact of integrated pest management (IPM) in reducing the insecticide residues is reviewed and presented in the following pages.

2.1 MONITORING PESTICIDE RESIDUES IN FOOD CROPS, COTTON, VEGETABLES, SOIL AND WATER

2.1.1 Monitoring Pesticide Residues in Rice

Following the application of 10% technical HCH dust at 2.5 kg a.i. ha^{-1} on rice crop at the flowering stage, residue determined in soil and various organs of the rice crop at harvest time indicated the presence of maximum residues in the rice bran, followed by straw, husk and rice grain. Boiling of the rice grains did not result in any reduction of HCH residues (Battu *et al.*, 1989).

Wanleelag and Ngarmpongsai, (1990) reported that rice seeds collected from local markets of selected provinces in Thailand were found to be contaminated with 0.03-2.0 μg kg^{-1} of DDT, 0.05 μg kg^{-1} of carbofuran and the

concentrations of the insecticides were below the tolerance level allowed by WHO/FAO.

Rice samples collected from different parts of Tamil Nadu, India were monitored for the presence of HCH, DDT and Malathion; and the samples were found to be contaminated with isomers of HCH and to a lesser extent with DDT. The mean level of residues was 0.001 mg kg^{-1}. Malathion was not detected in any of the samples analysed (Kannathasan and Regupathy, 1992).

Monitoring the samples of rice and wheat from the market for HCH and DDT in Bangalore, Karnataka, India, showed that all the rice and wheat samples were contaminated with 0.0049-0.0505 and 0.0034-0.9312 mg kg^{-1} HCH, respectively; and no DDT residues were detected in the samples (Ahuja and Awasthi, 1993).

Rice grain samples from Haryana, Maharashtra, West Bengal, Bihar, Orissa, Kerala, Tamil Nadu and Gujarat (1989-90) monitored under the AICRP on pesticide residues revealed that 85-100 per cent of the samples were contaminated with HCH (Kathpal and Kumari, 1993).

Chinnaiah *et al.* (1998) reported that the residues of lindane 20 EC and lindane dust when applied to rice crop at 500 g and 1000 g a.i. ha^{-1} at panicle emergence and milky stage recorded residues above the MRL in paddy straw at both the concentrations, but chlorpyriphos applied at the same concentration showed below the MRL residues in all paddy fractions.

The lindane residues were below MRL (0.25 mg kg^{-1}) in various parts of the rice crop, except in the case of straw, and lindane dust application resulted in residues of 0.2531 and 0.4616 mg kg^{-1} at 500 and 1000 g a.i. ha^{-1}, respectively. Quinalphos AF and chlorpyriphos EC @ 500 and 1000 g a.i. ha^{-1} recorded residues below the detectable limit and below the MRL, respectively in all the paddy fractions (Narasimha Reddy *et al.*, 2000).

An analytical method for the determination of 47 organophosphate pesticides in rice using solid phase extraction (SPE) cartridge for cleanup and analysed in GC-FPD (Gas chromatography-flame photometer detector) gave recoveries varying from 74% to 126%; and the detection limits ranged from 0.005 to 0.04 $\mu g\ g^{-1}$. Cleanup using SPE gave results comparable to or better than those obtained by the liquid-liquid extraction method (Chien *et al.*, 2000).

No detectable residue of betacyfluthrin was present in rice grain, husk, bran and straw after application of 0.122, 0.1875 or 0.375 g a.i. ha^{-1} in the *Rabi* season, but the residues were found in bran (0.4 $\mu g\ g^{-1}$) in the summer crop, which were below the tolerance limit (Nalini *et al.*, 2003).

Results of a study on the impact of pesticide residues in rice ecosystem indicated that pesticides moved off-site and could be present at low concentrations in drainage channels and associated creeks as observed by the adverse effects on indicator aquatic organisms (Kumar *et al.*, 2004).

Field studies conducted to investigate the persistence and dissipation pattern of BPMC (fenobucarb-O-sec-butyl phenyl N-methyl carbamate) applied at 0.75 and 1.5 kg a.i. ha^{-1} in rice ecosystem i.e. in soil, plant/straw, water, grain, husk

in West Bengal, indicated that about 99% of the residues had dissipated from the soil after 10 days and no residues were detected after 30 days in the soil and after 3 days in the water. The half-life values for the plant were 11.58 and 10 days for two different rates of application (Alam *et al.*, 2006).

Survey of pesticide residues in 343 samples of domestic rice and 32 samples of imported rice, showed the presence of 11 kinds of pesticides (including organophosphorus, organochlorine, carbamate, pyrethroid, organonitrogen pesticides and bromide) at levels between trace and 1 mg kg^{-1} in 47 domestic rice samples. DDVP (Dimethyl dichlorovinyl phosphate) and bromide residues were detected at levels between 0.01 and 5 mg kg^{-1} in 18 imported rice samples and the residue levels were below ADI values (Kobayashi *et al.*, 2007).

The Gas chromatographic method used for the detection of pesticide residues in rice and in seeds of rice plants revealed that 98 seed samples contained residues higher than the maximum value according to national standard and the detected pesticides were chlorpyriphos (in all 18 samples), triazophos (in 2 samples) and omethoate (in 1 sample). No correlation was found between the pesticide residues in the seeds and those in the rice; although a much higher amount of pesticide residue (from several folds to 30 fold) was found in the seeds (Yuping *et al.*, 2008).

Studies made on the dynamics between time and frequency of pesticide application and pesticide residues in the rice grain, showed that the residues in the rice grain increased with the application of pesticides and there was a positive correlation between pesticide residues and the dosage and application frequency of

the pesticides. All the pesticides used in the study were detected in the rice grain except for dichlorvos, and followed the order of triazophos > acephate > methamidophos > chlorpyriphos > imidacloprid. The per cent of residues in straw, rice hull and grain was 46.0, 36.6 and 17.4, respectively. Pesticides applied in the period before heading had significantly lower residues than that applied in the period after heading and when employed in the period after heading, the pesticide residues increased remarkably and there was a close relationship between residues and the storage period of rice. It was concluded that the variety of pesticide, the date, the dosage and frequency of employing pesticides were related with the security of rice grain (YunHui *et al.*, 2008).

Oxyflurofen, a post emergence herbicide, when applied to the rice crop at 240 and 500 g a.i. ha^{-1}, showed 0.01 and 0.03 $\mu g\ g^{-1}$ residues in the straw, 0.03 and 0.03 $\mu g\ g^{-1}$ in soil and 0.02 and 0.1 $\mu g\ g^{-1}$ in the rice grain (Sondhia, 2009).

2.1.2 Monitoring Pesticide Residues in Maize

Average initial deposits of endosulfan on the whole cobs of maize following the application at 0.05, 0.1 and 0.2% were 6.3, 11.5, 19.3 mg kg^{-1}, respectively and the residues decreased to 50% in 3-5 days and were below the detectable level after 11-20 days (Singh *et al.*, 1992).

A field experiment conducted to determine the effect of irrigation water sources (sewage water (SW), agricultural drainage water (ADW), Nile water (NW) and ground water (GW) on pesticide contamination in maize and wheat in heavy and light soils of Egypt, indicated no detectable amount of pesticide residues in the maize or wheat grain, except for HCH, p, p'-DDE and heptachlor in maize grain

and p, p'-DDE, heptachlor in the wheat grain. In heavy soil, all the detected pesticide residues in maize grain decreased according to irrigation water sources as follows: ADW>GW>NW>SW. In the light soil, maize or wheat grains were contaminated with p, p'-DDE and heptachlor and the detected residues varied according to irrigation water as follows: GW>SW>NW (Zidan *et al.*, 2005).

2.1.3 Monitoring Pesticide Residues in Pigeonpea

The levels of fenvalerate residues in pigeonpea grain in various treatments [3 emulsion sprays @ 0.005%, 0.01% and 0.02% and a dust formulation (0.4%) @ 25 kg ha^{-1}] were below the tolerance limit of 1 mg kg^{-1} as prescribed by FAO. The residues in the pod shells without grain were more than 1 mg kg^{-1} in all treatments except for the rate at 0.005%. Maximum residues in the pod shells were found when fenvalerate was applied in its dust formulation, indicating its slow dissipation and longer persistence in the pod shells (Patel *et al.*, 1990).

Harvest time residues of endosulfan and HCH in pigeonpea when applied with endosulfan at 0.007 or 0.14% and HCH at 0.2 or 0.4%, resulted in detectable residues of HCH only at the 0.4% rate (Dethe *et al.*, 1991).

Monocrotophos residues in green pods, grain and haulms of pigeonpea at harvest after the application at 0.5 and 1.0 kg a.i. ha^{-1} were 10.79 and 16.68 mg kg^{-1} initially for 2 dosages, respectively in green pods and fell to 1.14 and 1.43 in 15 days. Residues decreased to 0.02 and 0.05 mg kg^{-1} in the grain and 0.69 and 1.27 mg kg^{-1} in the haulms (Singh and Hameed, 1991).

Endosulfan at 0.14%, monocrotophos at 0.08% and quinalphos at 0.10% each 3 sprays at 20 days interval in pigeonpea controlled the pests effectively. High yields and high level of residues were obtained. The residues were more concentrated in the husk than in the grain and it was recommended that neither the grain nor the husk should be consumed following the application of quinalphos and monocrotophos, but the grain might be safely consumed after treatment with endosulfan (Senapati *et al.*, 1992).

Monitoring pulse samples from Hyderabad, Hapur, Haryana and Parbhani showed contamination with DDT and HCH. Black gram grain was contaminated with 0.01 mg kg^{-1} DDT. Horse gram samples were contaminated with HCH (0.11 mg kg^{-1}); DDT (0.02 mg kg^{-1}) and aldrin (0.03 mg kg^{-1}) in Andhra Pradesh (Anonymous, 1993).

Endosulfan applied at the flowering and pod formation stages by foliar spraying @ 350 and 700 g a.i. ha^{-1} revealed half-lives of 4.2 and 4.7 days on foliage and 5.8 and 5 days on pods for the two levels of treatments, respectively. The initial deposits of 22.85 and 41.15 μg g^{-1} were noticed on the foliage and the corresponding values on pods at the two treatments levels were 5.26 and 8.28 μg g^{-1}. The low initial deposits of the insecticide on pods as compared to foliage could be due to lesser exposure of the pods than the dense foliage to the spray as well as the small total surface area of pods than the leaves. The residues of endosulfan in soil at harvest were found to be below the detectable limit (Tanwar and Handa, 1998).

2.1.4 Monitoring Pesticide Residues in Cotton

Samples of cotton seed oil analysed for HCH and DDT residues from market in Anand, Gujarat, India showed that all the cotton seed oil samples were contaminated with different isomers of HCH. About 100% of samples of cotton seed oil samples were contaminated with p, p' -TDE and p, p'-DDT (Talati *et al.*, 1991).

Monitoring multiple pesticide residues in 250 samples of cotton seed during three crop seasons revealed that 74% of the samples were contaminated with 24 different pesticides/metabolites out of which 9 were organochlorine, 8 organophosphorus and 7 synthetic pyrethroid compounds. The MRLs exceeded in 41% of the samples and the most frequently occurring pesticides were cyhalothrin, dimethoate, DDT and its metabolites, endosulfan and monocrotophos (Parveen *et al.*, 1996).

Studies made with synthetic pyrethroid sprays for their residue accumulation in cotton showed that the fresh lint contained 0.05 and 0.06 mg kg^{-1} of fenvalerate and cypermethrin, respectively when applied at 75 and 150 g a.i. ha^{-1} of fenvalerate and cypermethrin at 50 and 100 g a.i./ha (Ramamoorthy and Kalavathi, 1992).

When endosulfan was applied to cotton at 700 and 1400 g a.i. ha^{-1}, the residues in seed and oil at the time of the first picking, were below the MRLs of 1 and 0.5 mg kg^{-1}, respectively (Battu *et al.*, 1992).

Average residues of the pyrethroid insecticides in cotton seed and oil at the recommended dosages i.e. cypermethrin at 50 g a.i. $ha^{-1}$of two consecutive pickings were below MRLs, whereas endosulfan application at 700 g a.i ha^{-1} resulted in the residues above the limits (Yadav *et al.*, 1993). The residues of betacyfluthrin were detected only in the cotton lint samples with average values of 0.30 and 0.40 mg kg^{-1} after six applications at 12.50 and 18.75 g a.i. ha^{-1} doses and the residues were not detected in cotton seed (Battu *et al.*, 1999).

The residues of cypermethrin (when applied at 50 and 100 g a.i. ha^{-1}) and ethion (when applied at 400, 800 and 1600 g a.i. ha^{-1}) in cotton lint following six applications each were 0.17-0.25 mg kg^{-1} and 0.18-0.62 mg kg^{-1}, respectively in the first pick and no residues were detected in lint samples collected at second pick and were also below the detectable level in seed. It could be because of direct contamination of lint from the last application. Binding of insecticides with cellulose present in the lint fibres and more surface area available in comparison to seed could also be other reason (Singh *et al.*, 2001).

In cotton seed, DDT residue ranged from 0.008-4.91 μg g^{-1}, aldrin residue from 0.03-2.31 μg g^{-1}, γ-HCH residue from 0.004-1.22 μg g^{-1} and the endosulfan residue from 0.007-1.76 μg g^{-1} (Hayat *et al.*, 2001).

Estimation of different insecticides in cotton lint samples collected from the cotton growing areas of Punjab using multi-residue method revealed that the majority of the samples were contaminated with endosulfan residues. Ethion and cypermethrin were detected in 80% samples. The residues of chlorpyriphos,

fenvalerate, traizophos, deltamethrin and profenophos were also present in 40, 28, 14, 8 and 8% of the lint samples, respectively (Blossom and Singh, 2004).

Estimation of harvest time residues of carbosulfan in cotton seed, lint, oil and soil after application at 250, 500 and 1000 g a.i. ha^{-1} at 15 days interval, showed that none of the samples had detectable amount of the residue with minimum determinable levels of <0.2mg kg^{-1} for lint, <0.01 mg kg^{-1} for seed, <0.03 mg kg^{-1} for oil and <0.01 mg kg^{-1} for soil (Rajeswaran *et al.*, 2005).

A study to determine the residues of different insecticides in 24 cotton samples, 12 each at first and second picking from Gujarat, revealed that out of the 24 lint samples, 23 were contaminated. Endosulfan was detected in all the 12 (Tr, Trace to 1.066 μg g^{-1}) and 11 (Tr to 2.506 μg g^{-1}) samples of lint for the first and second picking, respectively. Low levels of cypermethrin ranging from Tr to 0.091 μg g^{-1} and lambda cyhalothrin from Tr to 0.087 μg g^{-1} were also detected in two and four lint samples. The residues of organophosphate insecticides were detected in three and eight lint samples at the first and second pickings, respectively. Chlorpyriphos was detected in as many as eight samples (Tr to 0.135 μg g^{-1}), followed by quinalphos in five samples (Tr), triazophos (0.139-7.026 μg g^{-1}), profenophos (Tr-0.078 μg g^{-1}) each in two samples and malathion (Tr) in only one sample (Diwan *et al.*, 2006).

The harvest time residues of acetamiprid 20 SP applied on cotton at 10, 20, 40 and 80 g a.i. ha^{-1} were found to be below the detectable level of 0.5 ng g^{-1} in lint, soil and oil (Suganya Kanna *et al.*, 2007).

2.1.5 Monitoring Pesticide Residues in Various Food Commodities in India

Food items have been extensively examined for pesticide residues in India and the reports of widespread contamination are evident. DDT residues estimated in wheat, rice, pulses and groundnut which are the major constituents of the diet of people of Gujarat, were found in the range of 0.8 to 19.12 $\mu g\ g^{-1}$ and were much higher than the permissible level of approximately 3 $\mu g\ g^{-1}$ (Annual Report NIOH (National Institute of Occupational Health), 1976). Cereals and pulses showed mean concentrations of DDT and lindane of 2.1 and 2.6 $\mu g\ g^{-1}$, respectively, while the concentration of malathion in vegetables was 2.6 $\mu g\ g^{-1}$ (Mukherjee *et al.*, 1980).

Wheat (18) samples collected from Bombay market were contaminated with 0.5-0.8 $\mu g\ g^{-1}$ aldrin residues (KrishnaMurti, 1984). Raw materials of food stuffs (390 samples) collected from different markets in Calcutta were analysed for DDT, lindane and malathion. Ten samples each of cereals, pulses, green vegetables and fruits collected from Lucknow markets contained HCH and DDT residues higher in cereals compared to other food items (Kaphalia *et al.*, 1985).

A total of 224 samples of cereals, pulses, spices, vegetables, fruits, milk, butter, deshi ghee and edible oils analysed for the presence of organochlorine pesticide residues showed low or undetectable levels of pesticide residues in pulses, vegetables and fruit, and in contrast to very high concentrations in wheat flour, butter, mustard oil, deshi ghee, vegetable oil, groundnut oil and chilli.

The levels of HCH and DDT were low in other cereals and spices (Kaphalia *et al.*, 1990).

Earlier surveys, made in India, showed higher incidences of pesticide residues in the food commodities, mainly with organochlorine insecticides. Monitoring studies of the farmgate vegetables carried out in different parts of India (Madan *et al.*, 1996; Chahal *et al.*, 1997; Parihar *et al.*, 1997; Gupta *et al.*, 1998; Singh *et al.*, 1999), revealed contamination mostly with the organophosphorus and synthetic pyrethroid insecticides, indicating the changes in usage pattern from organochlorine to other groups of pesticides.

The All India Network Project on Pesticide Residues (AINP-PR) study on monitoring pesticide residues in agricultural produce and environmental samples indicated heavy residues during the 90's and the level and frequency of these residues have decreased over the years (Sharma, 2005).

Kumari and Kathpal, (2009) conducted a study to determine the contamination of vegetarian diet with organochlorines, synthetic pyrethroids, organophosphates and carbamate residues in homes, hotels and hostels in Hisar by using multiresidue analytical technique employing GC-ECD and GC-NPD (Gas chromatography-nitrogen phosphorus detector) and found that ADI of lindane in two and endosulfan in four samples exceeded the limits. Residues of other pesticides were found lower than the ADI limits of the respective pesticides. This could be attributed to use of lindane and endosulfan insecticides in almost all the agricultural crops.

2.1.6 Monitoring Pesticide Residues in Vegetables by Market basket and Farmgate Surveys and from Supervised Trials in Different Parts of the World

A study conducted to investigate the persistence of malathion, pirmiphos methyl and diazinon in some vegetables (tomatoes, cucumbers, green peppers, aubergines, okra, cabbage and snap beans) in Egypt, indicated that the residues increased withincreasing number of applications; initial deposits ranged between 2.2-2.8 and 2.4-4.1 mg kg^{-1} fruits after the first and third sprays, respectively. The highest amount of residue was detected in the malathion-treated fruits and the lowest amount in diazinon-treated ones. In all cases, the residues decreased progressively as time lapsed from the application of the treatment. Although the same amount of each insecticide was used on different crops, the residues differed from one crop to another. The period after which the sprayed crop could be harvested differed greatly depending on the number of sprays, the plant species and the insecticide used (El-Lakwah *et al.,* 1998).

Monitoring pesticide residues (methamidophos, chlorpyriphos, captan, chlorothalonil, endosulfan, λ-cyhalothrin and copper oxychloride) in irrigated tomato crops in four farms located in a high technology area in Sao Paulo, Brazil showed the residues of fungicides and insecticides during frutification and maturation stages (0.03-3.75 mg kg^{-1}) and those pesticides applied mainly during vegetative growth, were not found (Zavatti and Abakerli, 1999).

A market survey conducted to monitor some pesticide residues in fresh vegetables and fruits from local and public markets in Kalubia, Egypt during

December 1998 and January 1999 (winter) and June-July, 1999 (summer) showed that the pesticide residues varied according to season and crop. Organochlorines were the most detected contaminants. Fenitrothion, parathion, profenophos, fenpropathrin and s-fenvalerate were also detected from certain sites. The residues did not exceed the MRLs established by Codex Alimentarious Committee on pesticide residues with few exceptions. ADI (Acceptable daily intake) for chlordane and heptachlor epoxide were higher than the permissible levels (Zidan *et al.*, 2000).

A study conducted in 1990-91 for determining the contamination of food commodities in Pakistan, revealed a widespread contamination of vegetables and fruits with DDT (Dichlorodiphenyltrichloroethane) and γ-HCH (Hexachloro cyclo hexane). The levels of DDT in vegetables ranged from ND (Not detectable) to 8.6 $\mu g\ g^{-1}$ with the highest value in spinach, whereas γ-HCH ranged from 0.12 - 4.3 $\mu g\ g^{-1}$ with the highest level in the ladyfinger (Hayat *et al.*, 2001).

Detection of pesticide residues by multiresidue method in 138 fruit and vegetable samples from the fields in Brazil indicated that the 58.6% of fruit samples and 58.2% of vegetable samples were contaminated with pesticide residues. There were 19% of the samples that had residues of pesticides not registered for fruits and 41% for the vegetables (Gebara *et al.*, 2001).

In Nepal (Palikhe, 2002), about 900 samples of various food materials analysed between 1981 and 1986 showed different pesticide residues surpassing the legal limits in tea (malathion), grapes (methyl parathion), wheat flour (organophosphates), rice (HCH), chickpea (DDT) and organophosphates in

vegetables such as greens, potato, beans, cabbage, eggplant, garlic, chickpea and pumpkin. Pesticide residue contamination in various food crops during 1992-1996 was monitored and organochlorine pesticide residues in vegetables were reported to be low. Only a few samples of legumes were detected for DDT, which was found to vary in concentration from trace to 7.5 $\mu g\ g^{-1}$. In 14 samples of vegetables collected from the Kathmandu valley in 1998, the residue levels in cauliflower (0.75 $\mu g\ g^{-1}$), brinjal (2.66 $\mu g\ g^{-1}$) and red potato (2.66 $\mu g\ g^{-1}$) were above the ADI level (0.5 $\mu g\ g^{-1}$) as determined by Central Food Research Laboratory (CFRL).

The analysis of pyrethroid residues in vegetables using GC-ECD (Gas chromatography-electron capture detector) and GC-MS (Gas chromatography-Mass spectrometer) showed the presence of permethrin (2.0 mg kg^{-1}) in two samples of lettuce. In tomato, the residues of permethrin (8.6-18.8 mg kg^{-1} were confirmed in three samples and that of cypermethrin (3.0 mg kg^{-1}) in one sample. The levels of permethrin found in lettuce and tomato were above the maximum levels permitted by Brazalian legislation (0.1 mg kg^{-1} in lettuce and 0.3 mg kg^{-1} in tomato). Cypermethrin residues were detected in tomato, although its use was not allowed on this crop and the results showed that the good agricultural practices were not followed by some producers, suggesting the need to implement a monitoring program for the presence of pyrethroids in tomato and lettuce (Oviedo *et al*, 2003).

Pesticide residue studies made by Guerrero, (2003) in fruits and vegetables from specific areas of Columbia indicated high risk pesticide residues in tomato with two (4.7%) tomato samples showing residues above the MRL (Maximum residue limit).

Vegetables from Sao Paulo City of Brazil analysed for the presence of pesticide residues indicated that the samples with residue concentrations higher than the MRL and 1.1% and 20.9% of the samples had residues of the pesticides not registered for use on the commodity. Of the vegetable samples analysed, lettuce (82.6%), cabbage (56.2%) and tomato (46.1%) had the highest incidence of residues (Ciscato *et al.*, 2004).

Some 206 samples from 27 vegetables procured from retail markets of Karachi analysed for 24 pesticide residues, revealed that 63% of the samples were contaminated and 46% of the contaminated samples exceeded MRLs set by the FAO/WHO (Food and agricultural organization/World Health Organization). Approximately 49, 68, 72 and 62% of the samples were contaminated in 2000-2003, respectively showing an annual increasing trend. However, the MRL violation was found in 62, 56, 37 and 31% of the samples, respectively, showing an annual decreasing trend (Parveen *et al.*, 2005).

Experiments conducted in Pakistan to assess the residue levels of various insecticides in 179 samples of vegetables showed that none of the vegetables were free from the contamination of insecticide residues. About 17% of the samples were contaminated with methamidophos, 13% with cypermethrin, 7% with methomyl, 6% with chlorpyriphos, 5% with endosulfan, 2% with methidathion and 1% with lambda-cyhalothrin (Khan *et al.*, 2005).

Monitoring pesticide residues in 2223 samples (700 vegetables and 1523 fruits) in Sao Paulo City, Brazil from 1994 to 2001 revealed that 32.6% contained the residues of one or more pesticides. About 54% of the vegetable samples and

37% of the fruit samples had pesticide residues of less than 0.1 mg kg^{-1}. Multiple residues were detected in 5.8% of the vegetable samples and 11.4% of the fruit samples. Green bean, tomato, peach and strawberry had the highest incidence of multiple residues. Residues higher than the MRL were observed only in 3.0% of the vegetable and 0.9% of fruit samples (Gebara *et al.*, 2005).

A study undertaken to evaluate the decline of residues of benalaxyl, chlorothalonil and methomyl in processing tomato collected periodically until the end of pre-harvest interval (p.i.) following single chemical treatment (extraction with acetone and dichloromethane) by GLC (Gas liquid chromatography) showed that the residue concentrations after the p.i. were below the legal limits, nevertheless, the value for benalaxyl seemed to be rather high. The findings indicated the need for careful control of the spraying doses of the chemicals, in particular on varieties of tomato, which are used fresh (Gambacorta *et al.*, 2005).

The analysis of organochlorine pesticides with GC-ECD in vegetables from Nanjing suburb, China showed the residues of nine representative organochlorines in all the 10 vegetable samples analysed. DDT and HCH were the main residues accounting for 71.3-74.9% and 25.1-28.7% of the total residue levels detected, respectively and were below the MRL (JunLing *et al.*, 2006).

Fortification of tomato samples at different concentration levels (0.05 to 4.0 mg kg^{-1}) gave average recoveries ranging from 77 to 100% with relative standard deviation between 3.7% and 12.9% after extracting by matrix solid phase dispersion method and analysed using GC-MS with SIM (selected ion monitoring) option. Detection and quantification limits ranged from 0.01 to 0.02 mg kg^{-1} and

0.03 to 0.06 mg kg^{-1} for the whole fruit of tomato, respectively (Menezes Filho *et al.*, 2006).

The analysis of 28 multiple-class pesticide residues after extraction with acetone in vegetables (green pepper, red pepper and tomato) with GC-ECD and confirmation with GC-MS in SIM mode gave average recoveries of 67.3% and 123.3% with relative standard deviation (RSD) between 1.8 and 7.0% for all the analytes studied in pepper and tomato respectively. The detection limit varied from 0.1 to 2.6 μg kg^{-1} (Fenoll *et al.*, 2007).

A study conducted to evaluate chlorpyriphos, acephate, imidacloprid, dichlorovos and carbofuran residues in aubergine fruits using HPTLC (High performance thin layer chromatography) revealed that the samples were contaminated with all the pesticide residues except for the residues of imidacloprid. Pesticide residue contents were maximum at 0 DAT (days after treatment), followed by at 3 and 7 DAT. Residue quantity was negligible after 7 DAT and the fruits were suitable for consumption at 3 DAT (Iqbal *et al* , 2007).

A study conducted in Germany on pesticide residues in vegetables (628 samples in 2002 and 1500 in 2006) showed that the number of samples exceeding residue thresholds decreased from 12.7% (80 samples) to 2.1% (20 samples) during 2002-2006. Evaluation of pesticide residues before harvesting and within 2 days of harvesting of the produce allowed non-marketing of vegetables with high residue levels, thus improving consumer confidence in the products (Schietinger and Strohmeyer, 2007).

Nine pesticide residues in seven kinds of vegetables in wholesale, retail and supermarkets and vegetable production bases in Chongquing, China investigated quarterly during a whole year showed that the residues in the beginning of the year were higher than those in the later part of the year. The pesticide residues on vegetables from the market were higher than those from the vegetable production bases. The safety indices of vegetable quality were higher than 1.0 in the second and third quarters, and the safety was a certain risk (Yong *et al.*, 2007). Study conducted to investigate the organochlorine and pyrethroid residue from market in Malaysia revealed that 38 of the 302 vegetable samples were contaminated with cypermethrin with a mean value of 0.47 mg kg^{-1} and a range of 0.16 to 1.48 mg kg^{-1}. The mean values for all vegetable samples were below MRLs, allowed by the Malaysian Food Regulations, except for brinjal (Zawiyah *et al.*, 2007).

Tomato samples collected from different locations of Bangladesh to determine the presence of some selected organophosphorus and carbamate pesticide residues, analysed by HPLC (High performance liquid chromatography), showed that majority of the samples were found to be free from pesticide residues and some samples out of the 18 were found to be contaminated with chlorpyriphos, diazinon and carbaryl residues and the residues were in the range of 0.107-0.342, 0.157-0.381 and 0.1-0.32 mg kg^{-1} respectively, which were within the FAO/WHO guideline value of MRL for tomato (Fardous *et al.*, 2007).

Monitoring the market foods in Shangai during 2006-2007 showed contamination with heavy metals, pathogens, organophosphorus and carbamate

pesticides (over standard rate of 4.4% and 2.4%) however, with overall low levels of contamination (Lei *et al.*, 2008).

A study conducted to determine the contamination and health risk hazards of organophosphorus pesticide residues in vegetables in Ghana, revealed that 42% of the tomato and 10% of eggplant samples were contaminated with ethyl-chlorpyriphos. Health risks were found to be associated with some pesticides analysed (Darko and Akoto, 2008).

2.1.7 Monitoring Pesticide Residues in Vegetables in India

The residue levels of chlorinated pesticides in vegetables from Ludhiana markets detected as early as 1970 were 0.44 μg g^{-1} in brinjal and 0.08 μg g^{-1} in tomatoes (Jaglan and Chopra, 1970). A survey in 1972 reported very high levels of HCH *i.e.*, 105-200 μg g^{-1} in leafy vegetables from Mysore markets (Visveswaraiah and Jayaram, 1972).

Studies on insecticide residues in locally marketed fruits and vegetables in Udaipur, Rajasthan showed that out of the 40 samples tested, 34 had residues exceeding the permissible limits (Saxena *et al.*, 1990).

Tomato fruits were safe for consumption (with a residue concentration of less than 2 mg kg^{-1}) by 2, 4, 7 days after treatment at 3 different endosulfan concentrations of 0.5, 0.7 or 1.0 kg a.i. ha^{-1} respectively (Singh *et al.*, 1991). While, the studies of Sangama *et al.* (1991) brought out that endosulfan sprayed on aubergines at 0.5 and 1.0 kg a. i. ha^{-1} at fruit formation persisted for 15 days with corresponding safety intervals of 15.97 and 14.89 days.

Vegetables from the market of Lucknow, Uttar Pradesh, India were found to contain 0.064-0.49 mg kg^{-1} of HCH, 0.001-0.1 mg kg^{-1} of DDT, 0.001-0.05 mg kg^{-1} of aldrin and trace amounts of endosulfan ranging from 0.00005-0.0009 mg kg^{-1} and the residues were below the MRL (Dikshit *et al.*, 1992).

Most of the vegetable samples collected from Delhi, Haryana, Punjab, Karnataka, Andhra Pradesh and Maharashtra have been found to be contaminated with DDT and HCH and a few were contaminated with aldrin, heptachlor and endosulfan (Kathpal and Kumari, 1993).

Monitoring pesticide residues in vegetables (2500 samples) conducted by 14 centers of the All India Coordinated Research Project (AICRP) on Pesticide Residues Coordinating centers *viz.*, Assam, West Bengal, Orissa, Maharashtra, Rajasthan, Haryana, Punjab, Himachal Pradesh, Gujarat, Kerala, Tamil Nadu, Madhya Pradesh, Delhi and Andhra Pradesh indicated that most of the samples had negligible quantities of pesticide residues and were within the permissible limits (Kathpal and Kumari, 1993).

Naik *et al.* (1993) reported that residues of endosulfan, phosalone and monocrotophos on brinjal degraded to a safe concentration after 2, 5 and 7 days, respectively after application. The total endosulfan in eggplant fruits was 1.74 mg kg^{-1} after 1 hour on the day of application (525 g a.i. ha^{-1}) and decreased to 1.39 mg kg^{-1} after one day and 97% dissipated in 15 days. Total residues reached a level of 2 mg kg^{-1} (MRL) within one day of application. The residues were more than 2 mg kg^{-1} up to three days after double dose (750 g a.i. ha^{-1}) of spray, which

means that eggplant can be consumed three days after the application of the double dose. Alpha endosulfan degraded faster than beta endosulfan, whereas beta endosulfan residues were observed to increase from 0 to 1 day at both concentrations of spray. The change in ration of alpha to beta endosulfan could be due to faster transformation of alpha endosulfan to endosulfan sulphate, while the conversion of beta endosulfan to endosulfan sulphate is slow in plants, which was also observed during chemical reaction in the laboratory and the conversion of alpha to beta was faster in plants than that of beta to alpha (Gopal and Mukherjee, 1993).

Field experiment carried out by Patel *et al.* (1994) on quinalphos residues sprayed at 0.05% on Brinjal and 0.5 and 0.1% on cabbage revealed that the safe waiting period was 2.1 days in brinjal and 2.5 and 4.2 days in cabbage for lower and higher doses, respectively.

Monitoring different insecticides applied during different growth periods in vegetables in Haryana, showed the residues of monocrotophos, quinalphos, BHC isomers, DDT analogues and endosulfan in cauliflower, cabbage and pea peel. One sample of cabbage contained 0.230 mg kg^{-1} of monocrotophos, which was above the MRL. The residues of monocrotophos and endosulfan were found in one sample of brinjal. Samples of green and red chillies were contaminated with aldrin and dimethoate, while phosphamidon and malathion residues were found in the green chillies only. Residues of dimethoate were found in tomato and the monocrotophos residues were below the detectable level in okra, bitter gourd and smooth gourd. A comparison of the data obtained with the earlier data revealed that the incidence as well as level of pesticides contamination of seasonal

vegetables has significantly declined in India, which can be probably be attributed to change in the usage pattern of pesticides and the during last decade, the persistent organochlorines have been replaced with easily degradable organophosphates (Madan *et al.*, 1996).

Vegetables monitored for selected pesticide residues, revealed the residues of α, β, γ isomers of HCH, endosulfan, monocrotophos, quinalphos, dimethoate and carbendazim in most of the samples. The residues of monocrotophos in tomatoes, brinjal and okras and those of carbendazim on French beans were found to persist over the prescribed maximum residue limit values (Ahuja *et al.*, 1997).

Periodic monitoring market and farmgate samples of different vegetables in and around Bangalore for pesticide residues, showed a widespread contamination with isomers of HCH (safe limits) and traces of DDT metabolites in the market samples. About 40% of farm gate samples were contaminated with endosulfan (safe limits) and monocrotophos (bioconcentrations) and synthetic pyrethroids had a lower residue profile (Awasthi and Ahuja, 1997).

Monitoring pesticide residues in farmgate samples of brinjal at Jaipur indicated that out of the 88 samples of brinjal collected, 13 samples contained insecticide residues above the MRL (Parihar *et al.*, 1997).

Ninety six farmgate samples, cauliflower (23), brinjal (30), okra (12), cabbage (6) and tomato (25) when analysed for the residues of insecticides applied to the crops in Punjab, revealed that about 67% of the samples were contaminated and only 7% of these contained residues were above the respective MRLs.

Sixty nine vegetable samples analysed for the presence of DDT and HCH showed that 35 and 71% samples were contaminated. The results indicated that the present pattern of insecticide use in vegetable does not seem to contribute towards excessive residues and it was concluded that the use of insecticides should be need based and recommended insecticides should be applied and proper waiting period must be observed by the producer before marketing the vegetables (Chahal *et al.*, 1997).

Farmgate samples of different vegetables (bottle gourd, cauliflower, cabbage and fenugreek) obtained from villages around Jaipur, Rajasthan, were found to contain insecticide residues and some of the samples contained residues that were above the MRL (Gupta *et al.*, 1998).

Monitoring market samples for pesticide residues in Andhra Pradesh clearly revealed that the vegetable samples were contaminated with pesticides (Ramesh Babu *et al.*, 1996). Jagadeshwar Reddy (1998) found cypermethrin (0.2 mg kg^{-1}) in the vegetables collected from farmers' fields around Hyderabad and Guntur. In vegetables collected from Srikakulam, endosulfan was detected, but the concentration was below the MRL.

Under a nationwide program of pesticide residue monitoring in vegetables in India, 114 samples were analysed for aldrin of which 39 (34.2%) were found contaminated at an average concentration of 0.03 $\mu g\ g^{-1}$ (ND-0.8 $\mu g\ g^{-1}$). Out of the 201 samples analysed for DDT, 85 (42.3%) contained an average concentration of 0.1 $\mu g\ g^{-1}$ (ND-1.09 $\mu g\ g^{-1}$) and out of the 777 samples analysed for HCH, 447 (57.5%) contained an average of 0.37 $\mu g\ g^{-1}$ (0.01-10.86 $\mu g\ g^{-1}$).

Out of the 109 samples analysed for lindane, 105 (96.3 %) contained on average concentration of 0.15 μg g^{-1} (0.01-0.63 μg g^{-1}), and out of the 422 samples analysed for endosulfan 332 (78.9%) contained on average 0.82 μg g^{-1} (ND-18.63 μg g^{-1}). In general, the percentage of sample containing pesticide concentrations above the MRL were 14% for endosulfan, 0.6% for HCH and 9.2% for lindane (Agnihotri, 1999).

The chlorpyriphos residues persisted up to 15 days in cabbage and 10 days in brinjal when applied at 0.04 and 0.08%. The half-life values were 1.0 and 0.3 days for cabbage and 0.4 days for brinjal for both the doses. The initial deposits of 0.474 and 0.789 μg g^{-1} in cabbage; 0.133 and 0.183 μg g^{-1} at 0.04 and 0.08% doses of application were recorded. Low levels of initial deposits on brinjal fruits and their faster dissipation could be attributed to comparatively lower insecticidal loading as the insecticide mainly falls on the leaves (Patel *et al.*, 1999). Out of the 50 samples of green chilli monitored from areas around Jaipur city in India, showed that 30 samples were contaminated with different insecticides, out of which 8 samples showed insecticide residues above the MRL (Singh *et al.*, 1999).

Studies undertaken to monitor commonly used pesticides (12 types) from Kanpur city in vegetable (23 types) and fruit (12 types) samples revealed that malathion was used abundantly on fruits and vegetables with higher concentration in vegetables. Moderate amounts of organochlorines were found in some vegetables and they were below the level of established tolerances. This could be due to dissipation of the residues between the farm and marketplace and the standard preparation techniques applied prior to the testing. The results also indicated that the fruits that are supplied from cooler parts of the country have

lesser concentrations of malathion compared to those produced in the tropical region (Sanghi and Tewari, 2001).

In a more recent survey in India, 16 centers examined 796 samples of vegetables including brinjal, cabbage, cauliflower, okra, chilli, tomato, bittergourd, beans and others, either collected from farmgate or from local market (ICAR, 2002). Out of the 796 samples, 485 (61%) were found to be contaminated, including 18 samples with endosulfan and 3 samples with γ-HCH above the MRL.

Market samples of seasonal vegetables monitored during 1996-1997 in Haryana, showed a 100% contamination with low but measurable amounts of residues. About 23% of the samples showed contamination with organophosphorous compounds above their respective MRL values (Kumari *et al.*, 2002).

Locally marketed samples of vegetables (potato, tomato, cabbage, cauliflower, spinach and okra) in Jaipur city, Rajasthan, India collected at the beginning, middle and end of seasons when assessed for the presence of organochlorines, most of the samples were contaminated with residues and some exceeded the limit of tolerance prescribed by WHO/FAO (Bakore *et al.*, 2002). Singh and Gupta, (2002) reported that out of the 162 farmgate and market vegetable samples collected in Jaipur, 91 were contaminated with different insecticide residues, with 4 samples, 2 each of brinjal and cucumber contained the residues above the MRL. Monitoring the pesticide residues in two districts of West Bengal in respect of pesticide last applied in 149 farmgate vegetable samples conducted by Kole *et al.* (2002) showed that about 50% of the samples were contaminated with various pesticides (0.01-2.23 mg kg^{-1}) of which 16% were

above the MRL and the frequency of contamination was maximum in chilli and okra (80%) and it was concluded that suitable waiting periods before marketing the produce and some household practices, which are effective in decontaminating most of the toxic residues need to be followed.

No sample contained residues of dicofol and endosulfan above the MRL. Beta-cyfluthrin residues in market aubergine fruits dissipated up to 90% after 15 days of treatment and the waiting period was 10 days with a half life of 4.80-5.00 days (Arora and Gopal, 2002).

Single application of two synthetic pyrethroids *viz.*, cypermethrin at 22.5, 45 and 75 g a.i. ha^{-1} and fenvalerate at 30, 60 and 112.5 g a. i. ha^{-1} and endosulfan at 525 g a.i. ha^{-1} on brinjal left initial deposits of 0.31, 0.58 and 0.93 μg g^{-1} of cypermethrin, 0.43, 0.55 and 0.94 μg g^{-1} of fenvalerate and 125 μg g^{-1} of endosulfan and residue levels fell below MRL at 7 days for the pesticides under study. From the rate of dissipation, it was understood that the synthetic pyrethroids dissipated faster than endosulfan. In terms of half-life, endosulfan had longer persistence than the synthetic pyrethroids (Duara *et al.*, 2003).

Monitoring 80 samples of winter vegetables during 1997-98 in Hisar, Haryana for pesticide residues, using GC-ECD and GC-NPD following multiresidue analytical technique, revealed a 100% contamination of the samples with low but measurable amounts of pesticide residues. The residue levels of organophosphorus insecticides were highest, followed by carbamates, synthetic pyrethroids and organochlorines. About 32% of the samples showed contamination

with organophosphorus and carbamate insecticides above their respective MRL values (Kumari *et al.*, 2003).

Monitoring study conducted to estimate residue levels of organochlorine, organophosphorus and synthetic pyrethroid insecticides in vegetable samples, showed that all vegetable samples were contaminated withinsecticides but only 31% of the samples had residues above the tolerance limit (Mukherjee, 2003).

Analysis of 84 farm gate samples of seasonal vegetables, carried out using GC-ECD and GC-NPD equipped with capillary columns by using a multiresidue analytical technique, showed that 26% of the samples contained residues above the MRL values. The contamination was mainly with organophosphates, followed by synthetic pyrethroids and organochlorines. Among the organophosphates, the residues of monocrotophos, quinalphos and chlorpyriphos exceeded the MRL value in 23% of samples. The residues of monocrotophos were higher than the MRL value in 3 samples of brinjal and one sample of okra, cauliflower and smooth gourd. The residues of chlorpyriphos were greater than the MRL in 3 samples of cauliflower and 8 samples of cabbage, and the residues of quinalphos were greater than the MRL in one sample each of okra and cauliflower. Among the synthetic pyrethroids, cypermethrin was the main contaminant and its residue exceeded the MRL value in one sample each of brinjal, okra and cucumber. Only aldicarb among the carbamates was detected in potato. The residues of some organochlorines i.e. HCH, DDT and endosulfan were found in all the samples, but did not exceed the tolerance limit (Kumari *et al.*, 2004).

Monitoring market samples of various vegetables and fruits across the country showed 40-60% of the vegetable and 40% of fruit samples contaminated with different pesticides (Awasthi, 2005). Studies conducted by Kumari *et al.* (2005) on monitoring the pesticide residues from farmgate vegetable samples of Ranchi indicated that out of 30 samples, 29 were found to be contaminated with endosulfan (0.002-2.54 mg kg^{-1}). Two samples of cauliflower (2.01 and 2.37 mg kg^{-1}) and three samples of brinjal (2.09, 2.54 and 2.44 mg kg^{-1}) each from three different places were found to have residue above the MRL (2.00 mg kg^{-1}).

Thirtynine market samples of seasonal vegetables (cauliflower, brinjal and okra) from different parts of Ranchi monitored for residues of endosulfan applied during their growth period showed that all samples were contaminated with endosulfan (0.002-2.47 mg kg^{-1}) and six samples showed residues above the MRL values. None of the okra samples were found to have residue above the MRL (Shashi *et al.*, 2005).

Analysis of summer and winter vegetable samples during 2002-2003 for pesticide contamination, carried out in GC-ECD, showed that the contamination levels of winter vegetables (average concentration of 4.57, 6.80 and 5.47 μg kg^{-1}, respectively for lindane, endosulfan and DDT) were found to be slightly higher than the samples taken during summer (average concentration of 4.47, 3.14 and 2.82 μg kg^{-1} respectively, for lindane, endosulfan and DDT). The concentrations of these organochlorine pesticides in summer and winter vegetables were well below the established tolerances, but continuous consumption of such vegetables even with moderate contamination level can accumulate in body and may lead to chronic effects that could be fatal (Mayank and Ajay, 2005).

Dikshit *et al.* (2005) reported that foliar treatment of 20 g a.i. ha^{-1} of deltamethrin on okra and tomato at flowering and fruiting and a repeat application after 15 days, resulted in initial residues of 0.58 mg kg^{-1} in okra fruits and the residues were non detectable after 7^{th} day, while in tomato, the residues were not detected after10^{th} day.

Residues of different insecticides on aubergine fruits harvested at 3 days after the last spray of cypermethrin 25 EC at 0.006% were below detection limit. Endosulfan 35 EC at 0.05%, monocrotophos 36 WSC at 0.05% showed residue deposits of 0.092 and 0.061 mg kg^{-1}, respectively (Deshmukh and Bhamare, 2006).

A supervised trial conducted by Ahuja *et al.* (2006) on the persistence of the residues of lambda cyhalothrin in brinjal showed that the residues reached below detectable level in both the formulations (2.5 and 5.0 EC) and safe pre-harvest intervals were 4 and 5 days for lower (15 g a. i. ha^{-1}) and higher (30 g a. i. ha^{-1}) doses, respectively.

The data generated from the monitoring program on pesticide residues in different commodities viz., milk, rice, vegetables, fruits, oil, fish, condiments, feeds and fodders, water and total diet in Tamil nadu showed that out of the 582 samples monitored during 1990-1995, 7.4% samples exceeded the MRL. The level of contamination decreased from 77.0 to 60.0% during 1996-2000 and to 31.7% during 2001-2005. Simultaneously, remarkable reduction occurred in the samples exceeding the tolerance limits from 7.4 to 4.3% during 1996-2000 and 1.2% during 2001-2005. During 2006-07, out of 400 vegetable samples analysed,

97 were found contaminated but none of the samples exceeded the MRL (Chandrasekaran *et al.*, 2008).

Investigation on the insecticide residues in vegetable (brinjal, cucumber, okra, ridge gourd and tomato) and water samples collected from Kothapally Adarsha watershed in Ranga Reddy district, Andhra Pradesh during the 2007 rainy and post-rainy seasons revealed the presence of monocrotophos (0.001-0.044 mg kg^{-1}), chlorpyriphos (0.001-5.154 mg kg^{-1}), cypermethrin (0.001-0.352 mg kg^{-1}) and endosulfan (0.001-0.784 mg kg^{-1}). The residues of monocrotophos and endosulfan were below the MRL in all the 59 vegetable samples analysed, while the residues of chlorpyriphos were above the MRL in 4 samples and cypermethrin in 2 samples, which could be due to the cumulative effects of the use of monocrotophos and endosulfan in the recent years. In general, the insecticide residue concentration increased over the season, which could be due to the cumulative effect of insecticide application during the vegetable growing season. The water samples also revealed the presence of pesticide residues, but they were below MRLs (Ranga Rao *et al.*, 2009).

2.1.8 Monitoring Pesticide Residues in Soil

Low vertical mobility of aldrin, HCH, chlordane and heptachlor was demonstrated in sandy loam soil in a long term experiment covering ten crop seasons. It was noticed that highest residue concentrations were present in the surface (0-10 cm) soil layer of the fallow plots but in the 10-20 cm layer of the cropped soils. Several factors including fertilizer application, irrigation, cropping

pattern and other agronomic and soil, water and crop management practices influence the dissipation of pesticides under field conditions (Singh *et al.*, 1991).

A survey conducted by Kawano *et al.* (1992) on paddy, tomato, cotton, wheat, mustard, tea, sugarcane, vineyard and urban soils from different regions of India showed that DDT and HCH concentrations were found to be higher in the upland soils and lower in the paddy field soils. The levels and percentage contamination of DDTs and HCHs showed the extent of environmental contamination caused by continuous usage of relatively persistent organochlorine insecticides in large quantities.

The most common residues in the soils were those of DDT and related compounds. HCH, DDT and aldrin applied to the soil @ 2.5 kg a. i. ha^{-1} accumulated over a period in the 10-20 and 20-40 cm depths of the soil profile (Rao *et al.*, 1994). Kimber *et al.* (1994) while working on the environmental fate of endosulfan sprayed on cotton found that the bulk of the pesticide remained in the top 5 cm layer in the cotton growing soils of Australia. Probably the sorption of endosulfan and its metabolites by the soil particles was strong due to their polar character, resulting in negligible downward movement with irrigation and rain water. Also, low water solubility is another probable reason for lack of downward movement in the soil profile.

Monitoring 344 tea samples from 108 Chinese tea gardens showed that the DDT residues in soils planted with precious cultivars were greater than in soils planted with ordinary cultivars. Leaves of the ordinary tea cultivars had relatively

greater DDT residues. There was a relationship between pesticide residues in soils and leaves, age of tea plants, elevation and soil depth (WeJiang *et al.*, 1997).

Field studies conducted to investigate the fate of endosulfan in bare cotton soil applied at 875 g a.i. ha^{-1} after 42 and 63 days after sowing revealed that the dissipation of the endosulfan residues occurred to the extent of 92-97% in the first four-week period and by 238 days about 99% of the residue had dissipated. The half-life of endosulfan varied from 39 to 42 days. The parent endosulfan metabolized to endosulfan diol, which remained confined to top 5 cm soil layer and dissipated within 28 days, whereas endosulfan sulfate persisted till the end of the experiment and was confined to the upper 0-10 cm soil layer. Volatilization loss in the fallow plot following hydrolysis of endosulfan because of the alkaline pH of the soil and irrigation water, and photochemical and microbial decomposition also contribute to the dissipation of the endosulfan residues (Kathpal *et al.*, 1997).

Monitoring the pesticide residues in soils under cotton collected from the 0-15 cm soil depth at different periods (after soxhlet extraction and analysed in GC-ECD) showed that residues were in the range of 0.1 to 0.4 mg kg^{-1}. Endosulfan degraded rapidly in the soil and changed to the sulfate metabolite (Luchini *et al.*, 2000).

Monitoring DDT and DDE residues in the soils of Mandya and Mysore, Karnataka using immunoassay and gas liquid chromatography, indicated that 13 out of 13 samples contained DDE residues, while 8 out of the 13 samples had

DDT residues. The average concentration of DDT varied from 0.4 to 4 mg kg^{-1} and that of DDE from 0.06 to 0.25 mg kg^{-1} (Harish *et al.*, 2002).

Monitoring the orchard soils and water bodies in the horticultural ecosystem in North Bangalore indicated the presence of carbofuran and deltamethrin residues in the soil samples with grape and mango orchards, respectively. Persistence of carbofuran, chlorpyriphos, dicofol and mancozeb residues was recorded in the fields with chilli; triazophos and monocrotophos in cabbage fields; carbofuran, quinalphos and monocrotophos in okra fields and quinalphos, chlorpyriphos and monocrotophos in tomato fields (Awasthi *et al.*, 2002).

Monitoring the pesticide residue in soil was carried out by 11 coordinated centers in India (ICAR, 2002). Soil samples were collected from cotton-wheat cropping systems, rice, local orchards and vegetable fields. A total of 224 samples analysed showed that most of the soil samples contained DDT, HCH and endosulfan in detectable levels. The contamination of soil samples in different cropping systems ranged from 0.005-0.049 mg kg^{-1} for DDT, 0.03-3.21 mg kg^{-1} for HCH and 0.002-0.03 mg kg^{-1} for endosulfan. These results indicate the role of cropping systems on the degradation and the residues levels of various insecticides.

Investigations and survey carried out to determine heavy metal pollution and pesticide residues in soils of Kuming area in Yunnan, China indicated the presence of heavy metals to a varying extent and organochlorines and organophosphates in low concentrations (JianJun *et al.*, 2004).

A study conducted to determine the spatial distribution of DDT and HCH in soils surrounding the Guanting Reservoir, Beijing, China showed that the total amount of HCH in the soil ranged from 0.0 to 7.3 ng g^{-1} and DDT ranged from 0.0 to 57.9 ng g^{-1}. Both the insecticides were more concentrated in the soil under orchards, followed by farm and fallow fields (Tieyu *et al.*, 2005).

A study conducted in different regions of Indonesia to examine pesticide residues in soils and farm products, showed pesticide contamination of the agricultural lands (organochlorines at 7.9-11.4 μg kg^{-1}, organophosphates at 0.6-2.6 μg kg^{-1}), animal feed, animal products and by-products of food crops, which appeared to be due to excessive use of pesticides during the preceding cropping season. Pesticide residues were not detected in the milk of dairy cattle fed on by-products of organic cabbage, but lindane was detected in the milk of dairy cattle fed on non-organic cabbages, which indicated that organic farming practices may reduce pesticidal use in the animal and agricultural products (Indraningsih *et al.*, 2005).

Cultivated soils, ditch sediments and water flowing from several farm areas in British Columbia, Canada sampled to quantify the residues of endosulfan and other organochlorines, showed varying amounts of endosulfan residues in soils (<0.02-5.6 mg kg^{-1} dry wt) and ditch sediments (<0.02-3.33 mg kg^{-1} dry wt) and other organochlorines in the range of <0.02-1.62 mg kg^{-1} dry wt in cultivated soils and <0.02-9.73 mg kg^{-1} dry wt in sediments and the concentrations of organochlorine pesticide residues (including endosulfan and its derivatives) detected in ditch water were three orders of magnitude lower than those found in the sediments and soils with an estimated mean total of 0.73 μg L^{-1}. Despite the

continuing use of endosulfan, a decline of 22% of this pesticide was found in crop soils compared to that of in 1991 and it is speculated that endosulfan normally used for the control of many agricultural pests is being replaced by alternative, newer organophosphate pesticides. The continuing use of endosulfan in varying quantities appears to have decreased inputs to the ditch water, which may be attributed to the selected use of minimum quantities of endosulfan by farmers. The inputs of endosulfan to water body depend on the insecticide concentration in the suspended particulate matter, which is transported. These factors vary from season to season and from year to year, depending on the climatic conditions and rainfall events that influence soil erosion, runoff and the amounts of suspended particulate transported during with the runoff water (Wan *et al.*, 2005).

Jha and Mishra, 2005 found that all the 32 soil samples analysed from different cropping systems (vegetable-, rice-wheat-, sugarcane- and pulse- based) in Bihar, India were contaminated with HCH, DDT or endosulfan or with all the three insecticides. Vegetable soils had the highest pesticide residue and pulse growing soils contained the lowest insecticide residues.

Tieyu *et al.* (2006) conducted a study to determine the effects of environmental factors on organochlorine pesticide residues in soils of the Guanting Reservoir area, China. The total soil HCH content ranged from 0.0 to 7.33 ng g^{-1} and total DDT ranged from 0.0 to 76.01 ng g^{-1} in top soil samples collected from 56 sites. Several environmental factors including land use, soil texture, soil taxonomy and microbial biomass were considered to be responsible for the organochlorine pesticide levels observed and the data provide some insight into the effects of environmental conditions such as soil formation, agricultural cultivation,

nutrient enrichment and other anthropogenic activities on the degradation of organochlorine pesticides in soils.

Soil samples collected from villages of Thiruvallur district, Tamil Nadu and analysed for pesticide residues, showed that they contained p, p'-DDT ranging from 0.9 to 10.3 $\mu g\ kg^{-1}$ and HCH derivatives such as α-HCH in the range of 0.9 to 43.6 $\mu g\ kg^{-1}$ and endosulfan sulfate was found in almost all the samples and in very high concentrations (Jayashree and Vasudevan, 2006).

Komal *et al.* (2006) reported that total endosulfan residues decreased by 86.6% during 78-292 days after its repeated applications to cotton. The residue concentration observed after 78 days of application was 0.88 ng g^{-1} dry weight of soil. At the end of 145 days, a 35% decrease in the quinalphos residue was observed, which declined further by 50.9% in 292 days.

A field study was conducted in the Taihu Lake region of China to determine the residues of 13 organochlorines in soils from Paddy fields, tree land and fallow lands. The concentration of organochlorines residues was higher in the agricultural soils than in the uncultivated fallow soils. DDT was in the highest concentration in all the soil samples and its concentration ranged from 3.10 ng g^{-1} to 166.55 ng g^{-1}, followed by HCH (0.73-60.97 ng g^{-1}). Dieldrin, endrin, HCH and alpha endosulfan were also found but their concentration was less than 15 ng g^{-1}. Ratios of p'p- (DDD + DDE)/ DDT in soils under three land usages were: paddy field > tree land > fallow land, indicating that land usage influenced the degradation of DDT in soils. The data showed that the ban on the use of HCH and DDT resulted in a tremendous reduction of these pesticide residues in soils, but

there are still high amounts of these residues in soils, which need remediation (Fang *et al.*, 2007).

2.1.9 Monitoring Pesticide Residues in Water in Different Parts of the World

Monitoring the residues of 72 pesticides in natural waters collected from surface river, irrigation channel and lake waters between February and July 1992 in Valencia, Spain revealed that no pesticide residues were present in 15 of the 40 water samples analysed. The mean number of pesticides detected in the remainder was about 4 per sample and the highest number was 9 (Pico *et al.*, 1994).

A study was conducted to test the quality of water from paddy fields in two areas one of which represented heavy use of chemicals and another with low use of chemicals in Thailand. The samples taken from the main irrigation canal, division irrigation canal, paddy field and Tha Chin River before planting (in April) and during transplantation of rice (in October) contained DDT and α-BHC. The residues at some sampling points were higher than the acceptable limit for surface water (Boonyawat and Kurdmemoon, 1996).

A study on the determination of endosulfan and some synthetic pyrethroids in water samples by micro liquid-liquid extraction and GC-MS in Spain gave recoveries of >93.0% at a fortification level of 5 ng ml^{-1} and their relative standard deviations were between 1.9 and 11.7% and the detection limit of each compound ranged between 3 and 35 pg ml^{-1} (Fernandez-Gutierrez *et al.*, 1998).

Analysis of pesticide residues in natural waters from various regions of Greece was undertaken. About 69 samples were analysed, 44 of which were intended for human consumption. Residues of 11 pesticides were detected in 13 water samples. The most frequently appearing pesticides were lindane and its isomer α-BHC. Since the use of these chlorinated pesticides has been banned in Greece for the last 20 years their appearance may be attributed to their use in the neighboring countries because the rivers run across several countries (Miliadis, 1998).

A study conducted by Ahad *et al.* (2000) to determine the residues of chlorpyriphos, endosulfan, dichlorvos and dimethoate in ground water of Mardan division, Pakistan, revealed that the contamination levels were below maximum acceptable concentration (MAC) set by the European Community, except for three sites namely Amber, Swabi (0.82 μg l^{-1}), Lahore shakh, Chota Lahore (0.50 μg l^{-1}) and Madras Kalay, Mardan (0.64 μg l^{-1}).

The concentration of γ-HCH residue in water samples from three lakes of the mid western region of Nepal ranged from 0.01 to 0.10 mg l^{-1} (Palikhe, 2002). Water and sediment samples collected from different lakes in Turkey for the presence of organochlorine pesticide residues, revealed that the residues were higher in the sediment samples than in the water samples. The highest average amounts of extractable α-BHC (benzene hexa chloride), heptachlor epoxide and β-BHC and lindane in sediment samples were 1.38 μg g^{-1}, 1.394 μg g^{-1}, 2.328 μg g^{-1} and 1.79 μg g^{-1}, respectively (Barlas, 2002).

Investigation to determine the contamination of ground and surface waters with endosulfan in three intensive agricultural areas in the Western Cape, South Africa revealed that the residues of endosulfan were widespread in ground, surface and drinking waters The contamination was mostly at low levels, but regularly exceeded the European drinking water standard of 0 1 μg l^{1} The presence of residues were more frequent in the surface water (47%) than in groundwater (32%) and coincided with irrigation and to a lesser extent to spraying and trigger rains (Dalvie *et al* 2003) Experiment conducted to determine the occurrence of HCH and DDT in Guanting Reservoir and Yongding River, China following the ban of organochlorines, showed that the concentrations of both the pesticides were below the MRL (Wang *et al* 2003)

A survey done to determine the presence of residues of organochlorine pesticides in surface waters of Northern Greece collected seasonally from river and five lakes for a period of two years, showed the presence of isomers of HCH, aldrin, dieldrin and endosulfan sulfate In some cases the concentrations detected were higher than the qualitative target levels set by the European Union (Golfinopoulos *et al* 2003) Water, sediment and soil samples collected from Southern Lake Victoria (nine districts of Tanzanian side of lake) and its basin and analysed for 76 organochlorine, organophosphorus, carbamate and pyrethroid pesticide residues, indicated that DDT and HCH were the only detected pesticides with concentration up to 1 6 mg l^{1} and 0 2 mg l^{1} in water, 600 mg kg^{1} and 132 mg kg^{1} dry mass in sediments and 20 mg kg^{1} and 59 mg kg^{1} dry mass in soil, respectively The higher levels of the residues were detected during the rainy season than in the dry season The study showed that despite the ban on DDT use

in agriculture in Tanzania since 1992, it was still being used in some districts at the basin and technical HCH was commonly used in the area inspite of its being de-registered (Henry and Kishimba, 2003).

A study conducted by Manirakiza *et al* (2003) to determine the residues of 21 organochlorine pesticides in 74 water, 76 soil and 160 vegetable samples from city farms in West Africa, revealed that the main contaminants were DDT in water (231.9 ng l^{-1}), soil (71.4 ng g^{-1}) and in vegetables (5.03 ng g^{-1}). Different bioconcentration factors for sum HCHs, sum DDTs and sum endosulfans obtained, confirmed the uptake and translocation of chemicals from soil to plant.

Evaluation of water quality of lagoon system in Southern Mexico during 2002 indicated the residues of DDD (2.0 µg l^{-1}) in water, DDE (247 ng g^{-1}) and endosulfan I (814 ng g^{-1}) in sediment samples. The spatial distribution of these contaminants implied major potential risks because the most polluted sites were found to be those with the highest fishing activity (Hernandez Romero *et al*, 2004).

An assessment of the residues of nine persistent organochlorine pesticides in water samples of the Ganges-Brahmaputra-Meghna estuary in Bangladesh during the dry (October to December, 1997) and wet (April-June, 1997) seasons showed that the presence of residues was found indiscriminate but the residues of endrin was absent in all the water samples. The levels of residues were higher in water samples during the rainy season and the concentrations were found to be higher than the FAO/WHO recommended permissible limits (Jabber *et al.*, 2005).

The study conducted to analyze pesticide residues in water and sediment samples at six locations in Volta Lake in Ghana, showed lindane and endosulfan residue concentrations <0.008 μg l^{-1} and 0.036 μg l^{-1} respectively, in water and at <2.3 μg l^{-1} and 0.36 μg l^{-1}, respectively in sediments and DDT and DDE at <9.0 and 52.3 μg l^{-1} respectively. The results showed no significant contamination of the lake, but more importantly confirmed the involvement of complex processes in the partitioning of the chemicals between sediment and water (Ntow, 2005). Monitoring pesticide residues in water and sediments of Lake Pamvotis, Greece during one year showed highest concentrations of most of the pesticides during May to July in both matrices. The maximum percentage of ecological risk was 10.3 and 51.8% for water and 17.2 and 70.6% for sediment, based on acute and chronic level, respectively and the results showed that pesticides exert a significant pressure on the aquatic system, especially for the chronic effect level (Hela *et al.*, 2005).

Residues of organochlorine pesticides in surface water, sediment and fish samples from Meric Delta, Turkey, analysed by GC, showed that all the analysed 20 pesticides were wide spread throughout the study area. Concentration was higher in fish than in water and sediment samples. Because of lower solubility of the organochlorines in water, it was expected that they wouldl preferably be adsorbed to sediment or bioaccumulated in fish (Erkmen and Kolankaya, 2006). The study carried out to assess the levels of pesticide residues in water samples collected seasonally from Meiliangwan Bay, China within a period of one year indicated the presence of low concentrations of organochlorine pesticides and relatively high concentrations of organophosphates (Na *et al.*, 2006).

After the implementation of risk reduction programmes for the use of pesticides, results from analyzes of surface and groundwater samples throughout Sweden over a 20-year period (1985-2005) showed that the incidence of samples with a total pesticide concentration above 0.5 $\mu g\ l^{-1}$ had decreased over the years, both in surface and ground waters. Especially, in surface waters having shorter pathways between the site of application and the receiving water body, there has been a notable decrease in the pesticide residue concentrations (Tornquist *et al.*, 2007). Determination of the levels of organochlorine pesticide residues in water samples from some rivers in Edo, Nigeria using GC-ECD showed that all the water samples were contaminated, except for the Ikoro River where water samples exhibited non-detectable levels of p' p-DDE and p' p-DDT. The organochlorine pesticide residues detected in water were also present in the fish but at higher concentrations, which could be due to lipophilic nature of these organochlorine pesticides (Ize-Iyamu *et al.*, 2007).

A study carried out in the Troia (Troy), National Park to determine the residues of widely used pesticides in water and soil samples showed that methoxychlor, alpha endosulfan, beta endosulfan and α-HCH and β-HCH were detected in water samples collected from 13 sites in 4 different water resources between May and August 2003, whereas HCH, ethion, endosulfan, captan, trifluralin and mancozeb residues were found in soil samples collected from 14 different sites at depths of 0-20 cm in August 2003. The residues of alpha endosulfan were higher than those of other pesticides and ranged between 0.079-1.8 $\mu g\ l^{-1}$ with an average of 0.369 in May and between 0-8.3 $\mu g\ l^{-1}$ with an average of 0.954 $\mu g\ l^{-1}$ in August. The dominant residue in the soil samples was

HCH (0-49 μg l^{-1}) with an average of 10.07 μg l^{-1}. It was concluded that the observed decrease in species and number of migratory birds in the region could be the result of the amount of pesticide residues in both water and soil resources, originating from intensive agricultural application of the pesticides (Yildirim and Ozcan, 2007).

A survey carried out in 40 vegetable farms (greenhouse and open-field conditions) in the Coastal area of the Lazio region, Central Italy, to determine the exposure of the environment to pesticides and to quantify the Environment Exposure to pesticides (EEP) in air, water and soil showed that EEP-air of all pesticides were higher for vegetables grown under protected cultivation in comparison to those recorded for open-field, whereas an opposite trend was observed for the EEP-soil and EEP-groundwater with the highest values recorded under open field conditions (Marucci *et al.*, 2008).

Water samples collected from cotton and rice growing municipal areas of Faisabad, Pakistan and analysed for the presence of DDT and metabolites revealed that DDT and its metabolites were found in all areas, but the residues were not found in all water samples. The residue concentration in the water samples analysed ranged from 0.017-10.6 ng ml^{-1} (Asi *et al.*, 2008).

Pesticide residues were monitored in water samples in Southern Brazil. The water samples were collected five times, three samples from river and four samples form Channel during the rice growing season. Results of analysis (using GC-ECD) showed that pesticide residues in water decreased from sowing to harvesting of the crop. It was also observed that a more number of samples were

contaminated with residues at the lowest point. Carbofuran was detected more frequently and fipronil was present in each of the 7 samples and beta-cyfluthrin was not detected at any site (Grutzmacher *et al.*, 2008).

A study conducted to ascertain the presence and subsequent amount of organochlorines and organophosphates in water samples (using GC analysis) from lagoons in Ghana indicated that water samples from 4 lagoons contained 2.64, 0.49, 0.30 and 1.36 mg l^{-1} of pesticide residues, respectively and this showed some level of exposure of pesticide which would be harmful to humans (Essumang *et al.*, 2009).

2.1.10 Monitoring Pesticide Residues in Water in India

In India, concentrations of aldrin ranged from ND (not detected) to 391 ng l^{-1}; DDT, ND-847 ng l^{-1}; dieldrin, ND-39 ng l^{-1}; heptachlor, ND-148 ng l^{-1}; HCH, ND-100000 ng l^{-1} and endosulfan, ND-98 ng l^{-1} in surface water samples. Drinking water samples from Lucknow contained DDT (7.5 ng l^{-1}) and HCH (7.8 ng l^{-1}) (Kaphalia *et al.*, 1985).

Water samples collected from the Vellar river and Pichavaram mangroves in Tamil Nadu, India were found to contain HCH and DDT residues in higher concentration during October to February, in particular those of HCH, which reflected its frequent use (Ramesh *et al.*, 1990). All the isomers of HCH were detected and γ-isomer was predominant among the residues measured. The total DDT concentration ranged from 10.9 to 315 ng l^{-1}. Some earlier reports from different cities of India showed higher concentrations of chlorinated pesticides in water samples (Dikshit *et al.*, 1990).

In water samples from Ahmedabad, the levels of total HCH ranged from 23.9 to 248 ng l^{-1} with a mean concentration of 257 ng l^{-1} (Jani *et al* 1991) Mahapathra *et al* (1994) studied organophosphorus residues in the Ganga river water and groundwater in rural areas near Farrukhabad in northern India Monocrotophos was detected in many water samples from the Ganga river (ND-99 mg l^{-1}), while malathion and monocrotophos were frequently detected in the groundwater samples (ND-140 mg l^{-1})

Concentrations of HCH isomers mid-stream in the river Ganges in India ranged from 0 11 to 100 µg l^{-1} with an average concentration of 12 µg l^{-1}, which was comparable to those reported for DDT metabolites (Nayak *et al* 1995)

The river, tank and canal water collected from four districts of Andhra Pradesh *viz* Krishna, Mahaboobnagar Godavari and Nellore was found to be contaminated with HCH residues The tank water from the Godavari district recorded highest HCH residues (50 98 µg l^{-1}), followed by River Krishna (50 69 µg l^{-1}), Godavari River (43 99 µg l^{-1}) and Krishna River (23 2 µg l^{-1}) in the Mahaboobnagar district Lindane residues were highest in the canal water from the Godavari district River Godavari recorded the highest residues of DDT (25 1 µg l^{-1}) Aldrin (including dieldrin) residues were recorded in the highest concentration in the canal water (27 8 µg l^{-1}) from Krishna district and the presence of these residues could be due their longer periods of persistence (Reddy *et al* 1997)

Levels of DDT and HCH monitored during March-November in five lakes located in the Nainital region of Uttar Pradesh showed varying

concentrations of the residues in each lake. Maximum and minimum concentrations were found during July and March, respectively. Residues of HCH in July (3.12-8.66 μg l^{-1}) were above the EC limit of 3 μg l^{-1}. Mean DDT residues in all lakes ranged from 6.05 to 31.34 μg l^{-1} and exceeded the WHO recommendations of 0.1 μg l^{-1} for drinking water. DDT and HCH residues were also recorded in the tap water and highest concentrations were recorded in lakes close to cultivated land (Dua *et al*, 1998).

Reports on the analysis of groundwater samples from India show low contamination with aldrin concentrations at ND-40 ng l^{-1}; DDT, ND-701 ng l^{-1}; HCH, ND-118 ng l^{-1}; endosulfan, ND-22.1 ng l^{-1} (Kumar *et al*, 1995) dieldrin, ND-18 ng l^{-1} (Rao and Rao, 1999) and heptachlor, ND-112 ng l^{-1} (Singh, 2001).

In studies conducted under the ICAR (2002) under the AICRP on Pesticide Residues, the Monitoring groundwater (open well and tube well) and surface water (canal, pond, lakes) for pesticide residues was carried out by 16 coordinated centers. Of the 330 groundwater samples collected, 102 were found to be contaminated with DDT (traces to 0.83 μg l^{-1} concentration), 195 were contaminated with HCH (traces-4.22 μg l^{-1}) and 58 were contaminated with endosulfan (0.0025-1.3 μg l^{-1}). Out of the 280 surface water samples analysed, 126 were contaminated with DDT (traces-2.10 μg l^{-1}), 181 with HCH (traces-3.41 μg l^{-1}) and 73 with endosulfan (traces-2.88 μg l^{-1}).

The picture of persistent organic pollutant (POP) pesticides in Indian rivers showed levels of DDT, HCH and chlordane in the Yamuna river in Delhi of 660, 120 and < 0.008 ng l^{-1}; in Cooum Chennai of 250, 1.6, 1.0 ng l^{-1}; in Ulsoor

Bangalore of 13, 3.1 and 0.54 ng l^{-1}; in Mandori Goi of 18, 1.1, 0.035 ng l^{-1}; and Hoogly Calcutta of 6.2, 1.5, 0.180 ng l^{-1} respectively (Anbu, 2002). Monitoring water bodies in the horticultural ecosystem, North Bangalore, indicated the residues of HCH, DDT, dicofol, quinalphos, triazophos and chlorpyriphos in lake water samples. In open well water samples, HCH, DDT, dicofol, triazophos, carbofuran and phorate were observed. Bore well water samples contained only α and β-HCH residues and the detected residue levels were below the prescribed MRL in all the water bodies (Awasthi *et al.*, 2002).

In India, rainwater samples from the first and second rain of the season were collected and were analysed by 11 centres of ICAR. Of the 67 samples collected, 21% contained DDT (0.01-20.06 μg l^{-1}), 36% contained residues of HCH (0.013-3.92 μg l^{-1}) and 30% contained residues of endosulfan (0.01-3.02 μg l^{-1}). However, in Bangalore, Bhubaneshwar, Coimbatore and Hyderabad, no pesticide residues were detected in the rainwater (ICAR, 2002). Water samples collected from different parts of Uttaranchal analysed for chlorpyriphos, endosulfan, deltamethrin and fenvalerate residues, showed 0.13, 0.14, 0.01 and 0.06 mg ml^{-1} mean levels, respectively (Misra *et al.*, 2003).

Surface water, sediment and mature River Shad samples from the Bay of Bengal analysed for pesticide residues indicated that all the samples contained DDT group, lindane and heptachlor but the concentrations were lower than the permissible limit recommended by FAO/WHO, 1993 and a positive correlation existed between organochlorine pesticide residue concentration in water and sediments (Das and Das, 2004).

The organochlorine pesticide residues investigated in the water and fish flesh from sewage fed bheri (fresh water) and a flood plain wetland in West Bengal showed that DDT and HCH residues and metabolites disturbed the aquatic systems. HCH metabolites were higher in the bheri water than in the flood plain water (Samanta *et al.*, 2005).

A multi-residue method for the estimation of 14 pesticides belonging to organochlorine and organophosphorus groups in water, after extracting with dichloromethane and analysed with GLC-ECD, showed 80% recoveries at 0.1 and 1.0 μg l^{-1} for the 12 pesticides (Gupta *et al.*, 2006).

Water samples collected from 28 domestic well supplies in the Hyderabad city, India and analysed for organochlorine pesticide contamination, indicated that all the samples were contaminated with the four pesticides namely DDT, beta endosulfan (0.21 and 0.87 μg l^{-1}), alpha endosulfan and lindane (1.34 and 2.14 μg l^{-1}) and the concentrations were above respective ADI values for humans (Shukla *et al.*, 2006).

A study conducted to determine the residues of organochlorine insecticides in groundwater of Thiruvallur district in Tamil Nadu, India, revealed that γ-HCH residue was found in the greatest concentration of 9.8 μg l^{-1} in open wells and the maximum residue (15.9 μg l^{-1}) of endosulfan sulfate was recorded in bore well and the concentrations of p, p'-DDT and o, p'-DDT were 14.3 μg l^{-1} and 0.8 μg l^{-1}, respectively. The high concentration and maximum usage of HCH indicates that despite the restriction, excessive and indiscriminate use of technical grade HCH and lindane still continues due to low cost and popularity of these

formulations among the farmers. The maximum concentration of DDT derivatives may be due to the neutral pH (6.5) and high organic carbon (2.1%) content recorded in that village which increases aqueous solubility of the insecticide. Moreover, the coarse textured soils in the area have high run-off and leaching potential of the residues to groundwater. The sandy loam type of soil allows water and dissolved chemicals to move downward quickly. The permeability of the geological layers of the soil also contributes to a greater contamination of the ground water. Though endosulfan is less soluble in water, the concentrations of endosulfan and its derivatives were high in groundwater samples, which could be due to accidental spills, spray drift, leaching and run-in (Jayashree and Vasudevan, 2007).

A study on the concentration and distribution pattern of organochlorine insecticide residues in water and bed-sediments of Gomti River (8 sites) collected seasonally over a period of 2 years revealed the presence of residues ranging between 2.16 and 567.49 ng l^{-1} and 0.92 and 813.59 ng g^{-1} in river water and sediments, respectively. The results, further suggested that the source of DDT contamination was the aged and weathered agricultural soils with signature of recently used DDT in the rive catchments (Malik *et al.*, 2009).

The samples of water, sediments, shrimps and fish species analysed for organochlorine pesticide residues (different isomers of HCH, DDT and endosulfan) in selected streams of the Cauvery River in Karnataka, showed that all the samples contained at least one of the pesticides analysed and the concentration of all the pesticide residues was greater in the sediments. This may be attributed to the pollution from large number of distilleries, sugar industries, anthropogenic and

agricultural activities throughout the year. Overall, the results demonstrate the accumulation of pesticide residues through food chain (from soil-water-sediments-microbes-crop, fish-human) and this is a serious matter of concern (Begum *et al.*, 2009).

2.2 EVALUATION OF THE IMPACT OF IPM IN REDUCING RESIDUES

2.2.1 Evaluation of the Impact of IPM in Reducing Residues in Different Parts of the World

Water analyzes from 6 commercial tomato packinghouse dump tanks in South Carolina revealed that metal and pesticide residues accumulate in the dump-tank water during daily operation, which varied from 0.03 to 7.3 mg kg^{-1}. The water that was used for tomato production with a weekly spray schedule, contained about 2 to 10 times the pesticide and metal residues found in water used for tomatoes grown under the IPM protocol with pesticide applications based on scouting reports, and it was concluded that the IPM field practices can reduce residues in tomato packinghouse wastewater (Rushing *et al*, 1995).

Investigation of pesticide residues in 30 kinds of vegetables, fruits and 20 kinds of organic cultivation crops in Tokyo showed the presence of 11 organophosphorus insecticides, 2 carbamate insecticides, 1 organochlorine insecticide and 3 organochlorine fungicides. The concentrations of different pesticides ranged from 0.01-1.4 mg kg^{-1} in 11 crops, 0.03-0.70 mg kg^{-1} in 6 crops and 0.01 mg kg^{-1} in 1 crop. Residues of organochlorine fungicides and carbamate insecticides were higher than the maximum limits in 4 organic crops with a concentration range of 0.04-0.21 mg kg^{-1} (Kobayashi *et al.*, 1996). Pesticide

residues produced by applying traditional treatment schedules or the IPM programs when compared for samples of tomato and fruits showed that IPM strategies generally brought about an improvement in the sanitary quality of the produce and the pesticide residues were lower than in the traditional schedules based on treatments at fixed intervals (Leandri *et al.*, 1996).

An investigation made on the reduction of pesticide residues by the IPM on vegetables in Indonesia suggested that using entomopathogenic viruses in combination with pheromone traps could reduce insecticide spraying by 85% in Shallots. Using an action threshold control approach, insecticide use was reduced by an average of 63% compared with the twice weekly spraying (Dibiyantoro, 1998).

The IPM schedule for the production of vegetables in Slovenia resulted in pesticide residues below the allowed values (Bavec and Zadravec, 1999). Economic analysis of environmental benefits of the IPM in the Philippines showed that the IPM practices on onions reduced the use of specific pesticides from 25 to 65%, depending on the practice and the projected adoption of the IPM practices, which varied from 36 to 94%. Estimated economic benefits varied from 231 to 305 pesos per person per cropping season (40 pesos=1 US $) (Cuyno *et al.*, 2001).

An analysis of pesticide residue data to quantify the differences in residues on fruits and vegetables from three different market categories [conventionally grown, integrated pest management IPM grown/ no detectable residues (NDR), and organically grown] showed that organically grown foods consistently had about one-third as much residues as conventionally grown foods

and about one-half as much residues as found in the IPM/NDR samples. Conventionally grown and IPM/NDR samples were also far more likely to contain multiple pesticide residues than were organically grown samples. Comparison of the specific residues on specific crops showed that the residue concentrations in organic samples were consistently lower than in the other two categories (Baker *et al.*, 2002).

Supriatna, (2003) reported that the number of insecticides applied on rice in Java by the non-IPM field school farmers was higher than those of IPM farmers' field school and eight pesticide residues were found in concentration below the MRLs as most of the farmers applied recommended insecticides.

A comparative study of the IPM and conventional farmers in the Northern districts of Bangladesh suggested that the productivity of the IPM rice farmers was not significantly different from the productivity under conventional farming. But as the IPM reduces pesticide costs with no countervailing loss in production, it appears to be more profitable than conventional rice farming and the study also suggested substantial health and ecological benefits (Hassan and Bakshi, 2005).

2.2.1 Evaluation of the Impact of IPM in Reducing Residues in India

Experiment conducted to study the insecticide residues of chlorpyriphos, cypermethrin and monocrotophos from the IPM and non IPM adopting fields of okra and brinjal showed that the residues of chlorpyriphos in the soil were 0.41 $\mu g\ g^{-1}$ before sowing and 4.22 and 1.14 $mg\ g^{-1}$ at harvest time in non-IPM and IPM fields of okra, respectively. The presence of chlorpyriphos in soil before

sowing of okra indicated the persistence of insecticide, which might have been sprayed in the previous seasons on okra or other vegetables; and increased residue concentration after harvesting of crop may be due to repeated sprays of the insecticide on the crop. In the brinjal crop, the chlorpyriphos residue was not detected in the soil samples of both IPM and non-IPM fields which may be due to the fact that the brinjal field was kept fallow for a long period before taking up the trial which resulted in the degradation of chlorpyriphos in soil. The residues of chlorpyriphos and cypermethrin on okra were found to be 0.1 $\mu g\ g^{-1}$ and non detectable in the IPM trials and 5.75 and 0.63 µg g-1 in the non IPM fields, while that of monocrotophos in brinjal fruits were found to be non detectable and 1.25 $\mu g\ g^{-1}$ for IPM and non-IPM fields, respectively which indicated that harvested produce from IPM trials were safe to consume as the residues of insecticides were either below their MRL or not detected (Arora and Singh, 2004).

Sardana *et al.* (2004), reported that the use of NSKE (Neem Seed Kernal Extract) along withinsecticides and other biological and mechanical practices as a part of the IPM package on eggplant resulted in increased yield and the harvested produce from the non-IPM package, which had higher amount (above MRL) of the residues of monocrotophos (1.25 mg kg^{-1}).

Residues of chlorpyriphos, monocrotophos and cypermethrin were 1.54, 6.72, 3.76 $\mu g\ g^{-1}$ in non-IPM fields of okra which were higher than those recorded for the IPM fields (Sardana *et al.*, 2005).

A study conducted to examine pesticide use pattern and adoption of the IPM practices in rice, vegetables and cotton in North India, revealed that in both IPM and non-IPM farms, the intensity of pesticide use was high and high-risk pesticides were being used. Among the IPM farmers, various cultural practices had widespread adoption as opposed to the low adoption of biological practices in all the crops. Estimated values of farmers' willingness to pay for pesticide hazard reduction indicated that a market existed for the environmentally friendly pesticides in the study areas (Singh *et al.*, 2007).

Soil, water and rice grain samples from field trials conducted under the IPM and non-IPM modules in Kaithal (Harayana) and Dehradun (Uttarakhand) analysed for the presence of pesticide residues indicated the residues below the MRLs in both IPM and non-IPM trials and the pesticide residues were found below the detectable limit in soil and water samples of Kaithal region, while the carbendazim residues were detected at 0.001 mg kg^{-1} in rice grains and in the range of 0.03-0.001 mg kg^{-1} in soil samples from the Dehradun region (Arora *et al.*, 2008). Studies conducted to analyze the residue of commonly used pesticides *viz.*, methyl parathion, chlorpyriphos, endosulfan, cypermethrin, fenvalerate, carbendazim, imidacloprid and carbaryl in the IPM and non-IPM mango orchards, detected residues at below the prescribed MRL in non-IPM samples while IPM samples were free from pesticide residues (Singh *et al.*, 2008).

Samples of okra and brinjal fruits collected from non-IPM and IPM fields in Raispur village, Ghaziabad district (Uttar Pradesh) and analysed for pesticide residues, revealed the residues of chlorpyriphos in the soil of 4.219 and 1.135 μg g^{-1} at harvest time in non-IPM and IPM fields, respectively of the

summer okra crop from initial value of 0.407 μg g^{-1} before sowing, while in brinjal crop, it was not detected in soils of any trials. The residues of chlorpyriphos and cypermethrin on okra fruit were observed to be 5.75 and 0.625 μg g^{-1}, respectively for non-IPM fields and 0.104 μg g^{-1} of chlorpyriphos for the IPM trials. The residues of cypermethrin and imidacloprid were not detected in the IPM trials while the insecticide concentrations were 0.28 and 0.78 μg g^{-1}, respectively in the non-IPM trials (Arora, 2009).

Comparison of the residues of monocrotophos, chlorpyriphos, endosulfan and cypermethrin in the IPM and non-IPM fields of tomato and cucumber showed 0-741% higher residues in the non-IPM tomato samples and 25-292% higher residues in the non-IPM cucumber samples. The residues in the IPM fields ranged from 0.004-0.027 mg kg^{-1}, while it was 0.005-0.106 mg kg^{-1} in the non-IPM fields. The presence of residues in the IPM fields may be due to the left over residues in the soil and water used for the crops before growing vegetables and the proximity of non-IPM fields to IPM fields (Ranga Rao *et al.*, 2009).

MATERIALS AND METHODS

CHAPTER III

MATERIALS AND METHODS

The field studies were conducted to monitor the insecticide residues in food crops (rice, maize, pigeonpea), cotton, vegetables, soil and water and to know the impact of Integrated Pest Management (IPM) in reducing insecticide residues. The laboratory experiments were conducted in Pesticide Residue Laboratory at the International Crops Research Institute for the Semi-Arid Tropics (ICRISAT), Patancheru, India.

The materials utilized in conducting the experiments and various methods employed during the course of these investigations are given hereunder:

3.1 MONITORING THE INSECTICIDE RESIDUES IN DIFFERENT CROPS, SOIL AND WATER IN KOTHAPALLY WATERSHED OF RANGAREDDY DISTRICT, ANDHRA PRADESH IN THE SEMI-ARID REGION OF INDIA UNDER FARMER'S INSECT PEST MANAGEMENT PRACTICES

3.1.1 Experimental Site

The field trials were conducted in the two adjacent villages *viz.*, Kothapally and Enkepally in the Ranga Reddy district (Andhra Pradesh). Kothapally (longitude 78°5' to 78°8' E and latitude 17°20' to 17°24') is a contact village

(Plate 1) of International Crop Research Institute for Semi Arid Tropics

(ICRISAT), which has watershed-based activities and has 845 ha (2006-07) land covering different crops *viz.*, maize (150 ha), sorghum (45 ha), pigeonpea (180 ha), chickpea (75 ha), vegetables (165 ha), cotton (190 ha) and paddy (40 ha). Enkepally village has an acreage of about 984 ha with rice (80 ha), cotton (120 ha) and vegetables (200 ha) as the main crops. Other crops like pigeonpea, chickpea and maize are also cultivated covering an area of 584 ha.

3.1.1.1 Crops selected for monitoring study

Insecticide residues were monitored in various crops grown in Kothapally and Enkepally villages. The crops selected for this study are food crops (pigeonpea, maize and rice), cotton and vegetables (tomato and brinjal). Among the vegetables, tomato and brinjal crops were selected for the study because they are grown intensively and are available through out the year in both the villages. In addition to crop samples, insecticide residues were also monitored in the soil and ground water samples from the respective fields.

3.1.1.2 Timing and number of samples collected for the monitoring study

Monitoring the insecticide residues in crops, soil and water samples was carried out in Kothapally and Enkepally villages during 2008 and 2009 covering summer (March/April/May/June), *kharif* (July/August/September/October) and *rabi* (November/ December/ January/ February) seasons.

Food crops and cotton were analysed for insecticide residues during *rabi*, 2008 and 2009. Vegetable (tomato and brinjal) samples were monitored during summer, *kharif* and *rabi*, 2008 and summer and *kharif*, 2009.

Five farmers from each village covering each food crop and cotton were chosen for sampling. During the *Rabi* (post-rainy) 2008 and 2009 seasons, grain samples were collected from 10 fields each of rice, maize, pigeonpea and in the case of cotton crop, 10 lint samples were used. Similarly, 10 soil and 10 water samples from the selected fields were collected. Grain (or lint in the case of cotton), soil and water samples were analysed for insecticide residues.

In each season, 3 tomato and 2 brinjal farmers were identified from Kothapally village at random and the samples for insecticide residue analysis were collected. A total of 45 tomato fruit, 30 soil and 30 water samples from tomato fields and 40 brinjal, 20 soil and 20 water samples from brinjal fields were collected and analysed during the period of the study (Plate 2-5).

With respect to the non-contact village, Enkepally, 2 tomato and 2 brinjal farmers were selected and a total of 30 tomato fruit, 20 soil and 20 water samples from tomato fields and 40 brinjal, 20 soil and 20 water samples from brinjal fields were collected.

3.1.1.3 Portion of the sample analysed, size of the sample and periodicity of sampling

The information pertaining to plant organ analysed, size of the sample collected and periodicity of sampling are presented in table 1.

Plate 1: Lay out map of Kothapally village

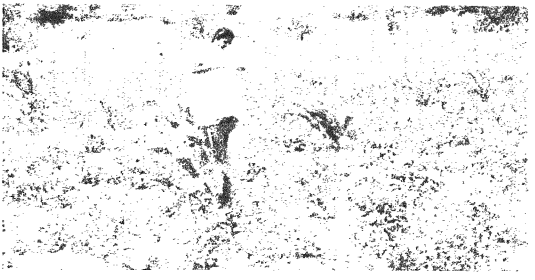


Plate 2: Vegetable sample collection for insecticide residue estimation

Plate 3: Soil sample collection for insecticide residue estimation

Table 1: Portion of the sample analysed, size of the sample collected and periodicity of sampling

Name of the matrix	Portion of the sample analysed	Size of the sample collected	Periodicity of sampling
Rice	Grain without husk	Five kilograms from 5 different locations	At harvest
Maize	Grain	Five kilograms from 5 different locations	At harvest
Pigeonpea	Grain without pod cover	Five kilograms from 5 different locations	At harvest
Cotton	Lint	Five kilograms from 5 different locations	At harvest
Tomato	Fruit	One to two kilograms from 10 randomly selected areas	At monthly intervals (thrice during the crop period)
Brinjal	Fruit	One to two kilograms from 10 randomly selected areas	At monthly intervals (four times during the crop period)
Soil		At each site, two soil plugs of about 15 cm deep and 3 to 5 cm diameter in grid pattern	At harvest for food crops and cotton. At the start and end of the crop season for vegetables
Water		Three liters from bore wells and open wells	At harvest for food crops (except maize)* and cotton. At the start and end of the crop season in vegetables

* Maize grown as rainfed crop and hence water samples were not collected from these fields.

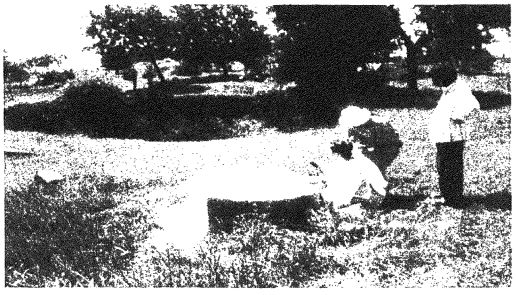


Plate 4: Bore well water sample collection for insecticide residue estimation

Plate 5: Open well chosen for water sample collection

Plate 6: Participatory rural appraisal on farmers' perception on plant protection

3.1.1.4 Storage of the samples

Polythene bags, glass bottles were used as containers for holding the samples of food crops, vegetables, soil and water and stored in deep freezer maintained at -10°C or below until analysed.

3.1.2 Participatory Rural Appraisal on Farmers' Perception on Plant Protection

Prior to conducting the monitoring study, Participatory rural appraisal (PRA) was undertaken in Kothapally and Enkepally villages to generate information on the existing plant protection practices and elicit farmers' views on plant protection approaches (Plate 6).

A questionnaire (Appendix) covering different plant protection aspects was developed. From each village, 25 farmers selected at random were interviewed to get the information on the plant protection practices followed by them during 2006, 2007 and their perception on various issues related to routine plant protection activities.

3.1.3 Extraction and Cleanup of Samples

3.1.3.1 Extraction of vegetable samples (tomato and brinjal)

Method used for the residue extraction from the samples was that based on multi-insecticide residues as several compounds could be targeted simultaneously. About 1-2 kg of the sample was chopped using knife and pooled together to get 100 g of homogenized sample for extraction. From the collected

sample, 100g of chopped or blended tomato or brinjal samples were blended with 200 ml acetone for 2 min at a high speed and homogenized in Polytron homogenizer (Plates 7 and 8), the mixture was filtered through Buchner funnel fitted with filter paper and this step was completed in less than 1 min with the help of Sonar® vacuum pump (Plate 9). Eighty milliliter of the filtered extract was transferred to a 1- liter (L) separatory funnel and extracted with 200 ml mixture of hexane: dichloromethane (1:1 v/v) by vigorously shaking for 1 min (Plates 10 and 11). The extract separated into two layers-- lower aqueous phase and the upper organic phase, depending on density gradient (Plate 12). The lower aqueous phase was then transferred to another 1 liter separatory funnel. The organic phase of the first separatory funnel was dried by passing through approximately 1.5'' sodium sulphate filled in a glass column (Plate 13). Ten milliliter of saturated sodium chloride solution was added to the separatory funnel with aqueous phase and was shaken vigorously for 30 sec. To the extract 100 ml dichloromethane was added and again shaken vigorously and the lower organic phase was dried by passing through same sodium sulphate that was used for drying organic extract of the first separatory funnel. Extraction was repeated with 100 ml dichloromethane once again and dried as above. Sodium sulphate column was rinsed with 50 ml dichloromethane to extract residue left in the column and the extract was concentrated using Buchi RE 121 rotavapor (Plate 14). Concentration step was repeated in the presence of hexane to remove all traces of dichloromethane and then repeated again to produce final extract in acetone solution. The solution was not allowed to dry in any of the concentration steps. The volume of the extract was adjusted to 2 ml with acetone (Luke *et al.*, 1981). The extract was cleaned by drawing it through syringe fitted with 0.45 teflon syringe filter (Plate 15 and 16).

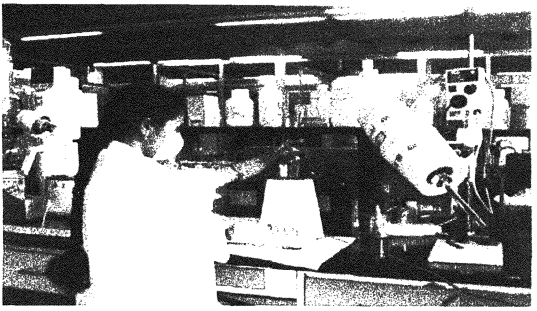


Plate 7: Blending of samples for extraction of insecticide residues

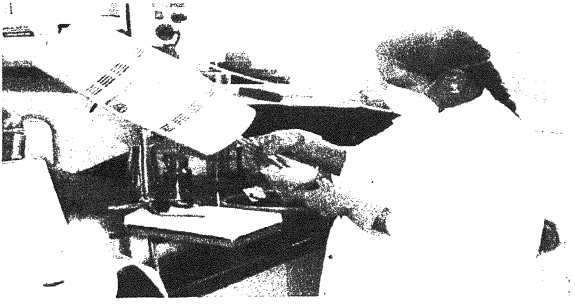


Plate 8: Homogenizing of samples in homogenizer

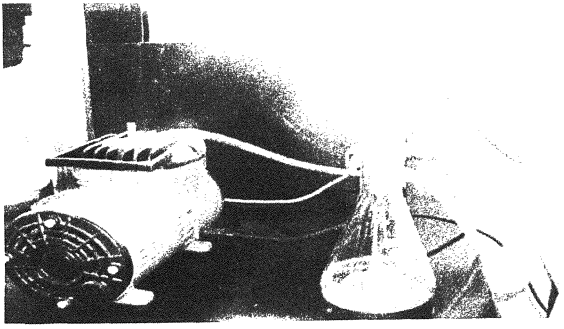
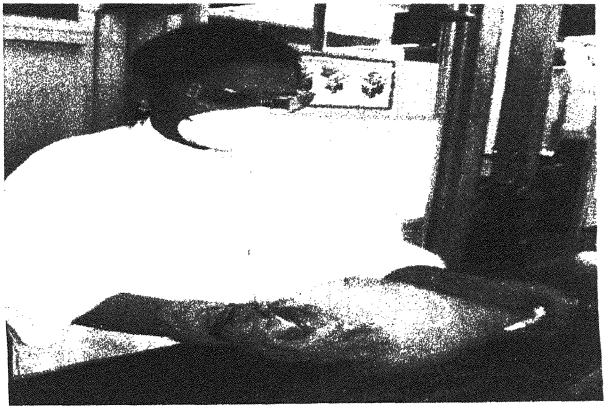


Plate 9: Filteration of homogenized sample with buchner funnel and vacuum pump

Plate 10: Extraction of filtered sample with hexane and dichloromethan



ate 11: Vigorous shaking of sample for separation of organic and aqueous layer

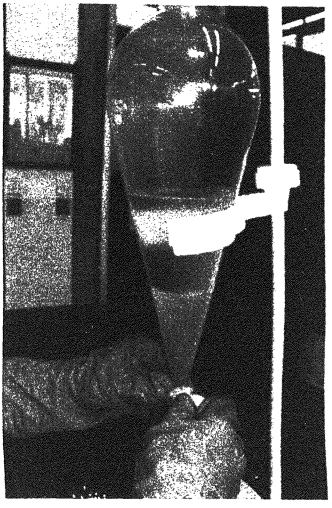


Plate 12: Separated upper organic and lower aqueous layers

13: Drying of organic solvent extract by passing through sodium sulphate column

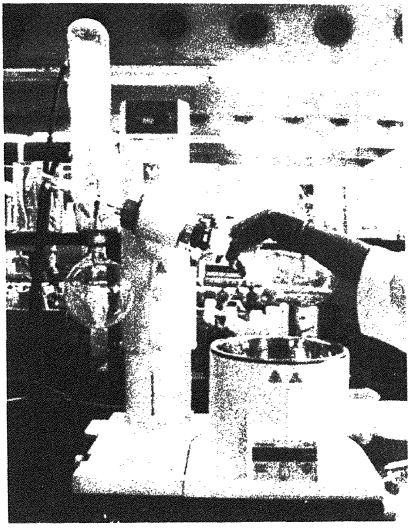


Plate 14: Concentration of organic solvent in rotovape

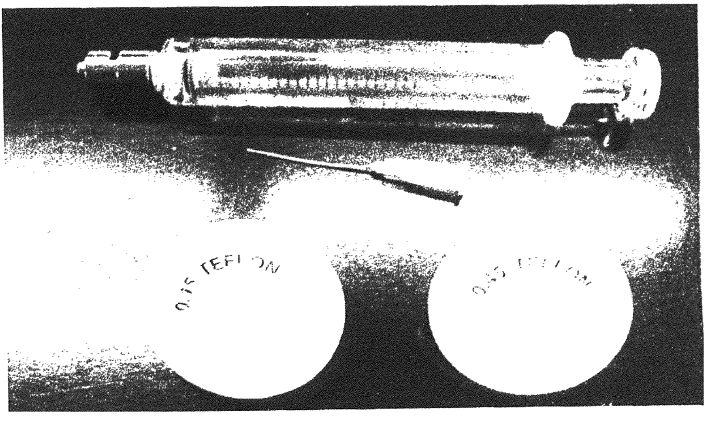


Plate 15: Syringe and filter used for cleanup of concentrated sample

3.1.3.2 Extraction of rice, maize, pigeonpea and cotton lint

Rice was pounded to separate grains from bran while maize grains were obtained by removal of husk. Pigeonpea grains were collected after removing pod cover. Fifteen grams of ground samples of rice, maize, pigeonpea and cotton lint (just soaked in acetone/water mixture) were blended with 350 ml acetone/water 65:35 for 2 min at high speed and the mixture filtered through Buchner funnel fitted with filter paper and this step was completed in less than 1 min with the help of Sonar® vacuum pump. Eighty milliliter of the filtered extract was transferred to one liter separatory funnel and extracted with 200 ml mixture of hexane: dichloromethane (1:1 v/v) by vigorous shaking for 1 min. The extract gets separated into two layers lower aqueous phase and upper organic phase depending on density gradient. The lower aqueous phase was then transferred to another one liter separatory funnel. The organic phase of the first separatory funnel was dried by passing through approximately 1.5" sodium sulphate filled in a glass column. Ten milliliter of saturated sodium chloride solution was added to the separatory funnel with aqueous phase and was shaken vigorously for 30 sec. To the extract 100 ml dichloromethane was added and again shaken vigorously and the lower organic phase was dried by passing through same sodium sulphate that was used for drying organic extract of the first separatory funnel. Extraction was repeated with 100 ml dichloromethane once again and dried as above. Sodium sulphate column was rinsed with 50 ml dichloromethane to extract residue left in the column and the extract was concentrated using Buchi RE 121 rotavapor. Concentration was done as mentioned under section 3.13.1 (Luke and Doose,

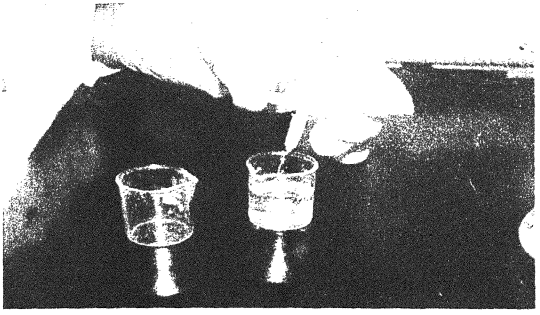
1983). The sample extract was cleaned by drawing it through syringe fitted with 0.45 teflon syringe filter.

3.1.3.3 Extraction of soil samples

The soil samples were dried at room temperature of 30°C. Visible twigs and stone pieces were taken out. The samples were then ground mechanically to obtain a homogenous powder and sieved through 2.5 mm mesh sieve. Ten gram of ground soil was taken and a few drops of liquid ammonia were added (to get all the adsorbed insecticides released from soil particles), mixed well and left for half an hour until ammonia evaporated. The soil was kept in a thimble after packing it in filter paper and put in soxhlet apparatus (Plate 17) and refluxed using hexane: acetone (1:1v/v) for 6-8 hours. Then the extract was concentrated and the final volume was made up to 1 ml with 10% acetone in hexane and later analysed in GC-MS (Vocenfe and Yolando, 2004).

3.1.3.4 Extraction of water samples

Five hundred milliliter of filtered water was transferred to one liter separatory funnel and 100 g of sodium chloride was added and shaken until dissolved. The residues were extracted thrice with dichloromethane (50:25:25 ml), each time shaking vigorously for one min and pressure was released intermittently. The lower organic layer was dried by passing through about 1.5'' sodium sulphate in a glass column. The organic layers were combined and concentrated with Buchi RE 121 Rotavapor. This concentration step was repeated thrice using hexane to remove all traces of dichloromethane and the final volume was made to 2 ml, which was analysed in GC-MS (Hernandez *et al.*, 1993).



ate 16: Cleaning of concentrated sample extract with Teflon syringe fi

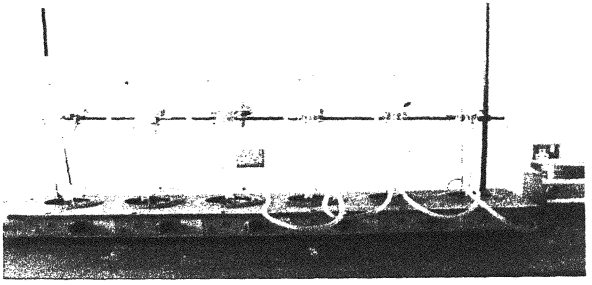


Plate 17: Soxhlet apparatus used for extraction of soil samples

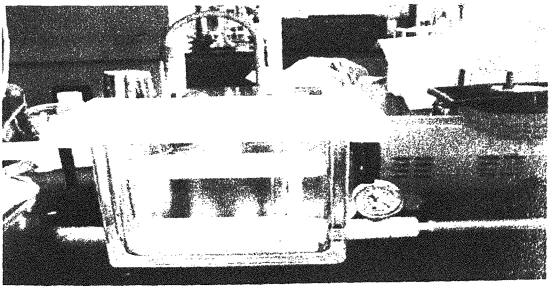


Plate 18: Cleanup of organic solvent extract with solid phase extraction c

to vacuum manifold

All the solvents used for extraction were of the analytical grade and supplied by Fischer Scientific/Qualigens, Mumbai.

3.1.3.5 Cleanup

Cleanup of the organic solvent extract prior to GC-MS determination was carried out to prevent deterioration of the GC column due to sample matrix co-extractant, to avoid interferences in the determination of insecticides at trace levels and to eliminate the matrix- induced enhancement effect.

Clean up of the extract was done with Solid Phase Extraction (SPE)-FL PR (florisil) cartridges fitted to SPE vacuum manifold (Plate 18), which were supplied by Phenomenex Company. The manifold consists of a clear glass chamber and a lid to which a vacuum is applied thereby drawing the sample through the SPE cartridge of filtration device. Adjustable racks placed in the glass vacuum chamber accommodate sample collection vessels. Lid assembly of vacuum manifold consists of four black legs attached to the underside of the manifold lid; needles attached to the male luer connection fittings on the underside of the lid. Stopcocks can be firmly inserted into the female luer fittings on the top of the lid and cartridge into the stopcock (Plate 19).

The vacuum manifold was attached to the Sonar® vacuum pump using 8mm ID thick wall vacuum tubing. Vacuum of 10 inches mercury was maintained by adjusting with bleed valve ring of the vacuum manifold. Then the cartridge was conditioned by running hexane through it. The sample was passed through the cartridge and pesticides were trapped into the sorbent material of the cartridge. Flow rate of sample was controlled by stopcocks. The rack assembly was kept inside the

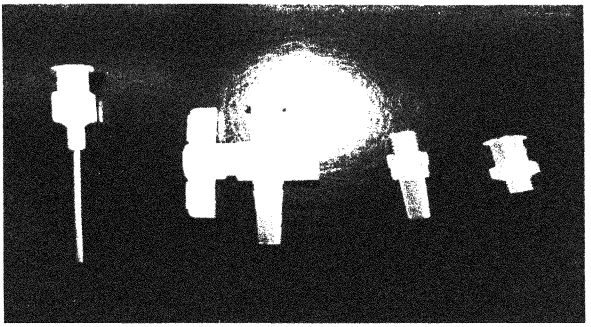


Plate 19: Parts of vacuum manifold

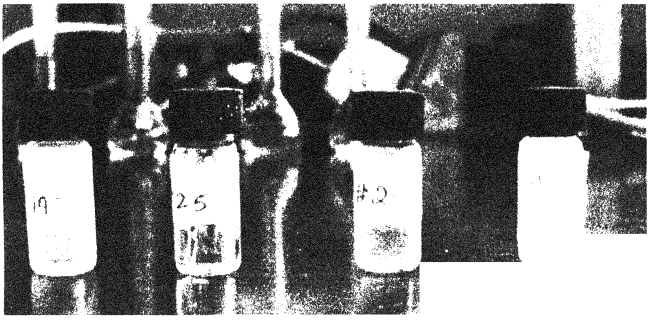


Plate 20: Samples ready for injection into GC-MS QP 5050 A

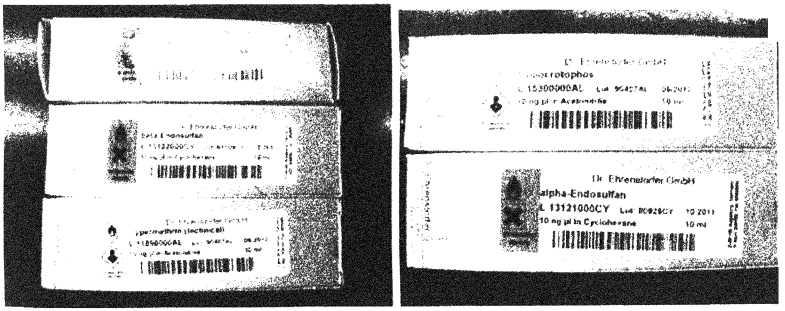


Plate 21: Insecticide standards used for preparation of insecticide mixtur

Chromatography (HPLC) grade solvents supplied by Fischer Scientific/Qualigens, Mumbai, were used in the preparation of standards (Plate 22).

3.1.4.1 Preparation of primary stock solution

A mixed 10 μg ml^{-1} primary stock solution was prepared by transferring 10 ml aliquot of 100 μg ml^{-1} stock solution into a 100 ml volumetric flask and the contents were made to the mark with hexane and the container was stored in refrigerator at 4°C.

3.1.4.2 Preparation of working solutions

Working solutions were prepared by diluting the stock standards to prepare calibration standard and fortification standards. Micropipettes and volumetric flasks, graduated test tubes were used to transfer the aliquots and for making up the volume throughout.

3.1.4.3 Preparation of calibration standards

The standard mixtures of analytes were prepared at 0.5 μg ml^{-1}, 0.2 μg ml^{-1}, 0.1 μg ml^{-1}, 0.05 μg ml^{-1} and 1.0 μg ml^{-1} concentrations by serial dilution technique for preparing the calibration curve. All the standards were always stored in refrigerator at 4°C.

3.1.5 Instrument Parameters

3.1.5.1 Gas chromatography - mass spectrometer analysis

Analysis of three groups of insecticides *viz.*, organophosphates (monocrotophos, chlorpyriphos), organochlorines (alpha and beta endosulfan) and synthetic pyrethroids (cypermethrin) was carried out on GCMS-QP 5050 A (Schimadzu Model) (Plate 23). GC-17A Ver.3 equipped with mass spectrometer detector and Zebron Multi residue column ZB -1, with 30 X 0.25 mm i.d. (internal diameter) and 0.25 µm thickness of 100% dimethylpolysiloxane stationary phase was used for estimation of all the above mentioned insecticides.

GC operating parameters were as follows:
Carrier gas: Helium
Column inlet pressure 130.1 kPa,
Column flow: 1.7 ml min^{-1},
Linear velocity: 48.7 cm sec^{-1},
Split ratio: 0,
Total flow: 3 ml min^{-1},
Carrier flow: 3 ml min^{-1}.

The column was initially maintained at 110 °C for 3 min, and then increased at the rate of 15 °C per min up to 280 °C. The column was held at 280 °C for 2 min and then the temperature was increased at the rate of 30 °C per min and finally increased to 300°C, at the rate of 30°C min^{-1} and held for 4 min to facilitate separation of all the compounds

The mass spectrometer parameters are summarized in Tables 2 and 3. The mass spectrometer was calibrated weekly. The individual insecticide standards

of monocrotophos, chlorpyriphos, alpha and beta endosulfan and cypermethrin (sum of four isomers) were run in scan mode. Later the same standards were run in selected ion monitoring (SIM) mode using two or three reference ions with total program time of 22.67 min.

Table 2: Mass spectrometer parameters

Acquisition mode	SIM
Micro scan width	0
Interface temperature	260°C
Solvent cut time	8.5 min
Detector voltage	0.1 kv
Threshold	1000
Interval	0.5 sec
GC program time	22.67 min

Table 3: Mass spectrometer program details

Start time (min)	End time (min)	Mass:charge ratio of base peak ions in mass spectrum		
		Chl1-m/z	Chl2-m/z	Chl3-m/z
5.00	10.00	127	67	97
10.00	12.20	97	197	314
12.20	13.75	241	195	160
13.75	17.20	163	181	165

Insecticides were identified according to their retention times, the target and qualifier ions and qualifier to target abundance ratios. The target and qualifier abundances were determined by injection of individual insecticide standard mixtures under the same chromatographic conditions using full scan with mass: charge (m/z) ratio ranging from 50 to 600 and also in SIM.

3.1.5.2 Preparation of the calibration curve

The standard mixtures of 0.05 μg ml^{-1}, 0.1 μg ml^{-1}, 0.2 μg ml^{-1} and 0.5 μg ml^{-1} concentrations (lower to higher concentration) were injected into GC-MS QP5050 A and the injection volume was 1 μl. A calibration curve or linearity curve was formed using the standard areas and retention times.

3.1.6 Repeatability

Repeatability expressed as Relative standard deviation (RSD) was calculated by injecting the same sample for five times. RSD was calculated by the formula

$$RSD = \frac{\text{Standard deviation}}{\text{Mean}} \times 100$$

3.1.7 Limit of Quantification (LOQ)

It is the lowest concentration tested at which an unambiguous identification of the analyte can be determined with acceptable mean recovery with an acceptable relative standard deviation (RSD). In order to obtain LOQ, samples were spiked with different known amounts of standard mixtures and the level at which acceptable recovery and RSD were obtained was considered as LOQ.

3.1.8 Limit of Detection (LOD)

It is the lowest amount of an analyte in a sample that can be detected but not necessarily quantitated as an exact value. It is generally three times less than

that of LOQ. LOQ = 3 LOD. Limit of detection in all the matrices were calculated based on LOQ values of the method.

3.1.9 Recovery experiments

Recovery experiments provide information on both precision and trueness and thereby the accuracy of the method. Recovery studies were carried out to establish the reliability of the analytical method and to determine the efficiency of extraction, portioning and cleanup steps by fortifying the substrate with known quantities of analytes.

Fortification of the untreated vegetables (tomato and brinjal), paddy, maize, pigeonpea, cotton lint, water and soil samples was conducted to determine the per cent recovery within each type of sample matrix for monocrotophos, chlorpyriphos, alpha and beta endosulfan and cypermethrin.

Recovery studies were done at two levels in all the matrices studied. LOQ for each individual matrix was considered as one level and the other is 2.5 or 5 times that of LOQ. Spiking was done at LOQ level of 0.005 $\mu g\ g^{-1}$ and five times of LOQ in vegetables (tomato and brinjal), at 0.01 $\mu g\ g^{-1}$ (LOQ), 0.025 $\mu g\ g^{-1}$ (2.5 times of LOQ) in paddy, maize, pigeonpea, cotton lint and soil and at 0.001 $\mu g\ ml^{-1}$ (LOQ) and 0.0005 $\mu g\ ml^{-1}$ (five times of LOQ) in water. Fortification of control was conducted in triplicate within sample sets. A control sample which was assumed to be untreated was compared.

3.1.9.1 Fortification of vegetables (tomato and brinjal)

A 100 g of vegetable sample was blended and 250 µl and 50 µl of 10 µg ml^{-1} of stock was added to get the fortification level at 0.025 µg g^{-1} and 0.005 µg g^{-1}. The extraction, cleanup procedure was followed as mentioned under section 3.1.3.

3.1.9.2 Fortification of rice, maize, pigeonpea, cotton lint and soil

A 15 g of ground rice, maize, pigeonpea grains, cotton lint and soil were fortified with 37.5 µl and 15 µl of 10 µg ml^{-1} of stock to get the fortification level at 0.025 µg g^{-1} and 0.01 µg g^{-1}. The extraction, cleanup procedure for rice, maize, pigeonpea and cottonlint was followed as mentioned under section 3.1.3.2 and that for soil as mentioned under section 3.1.3.3.

Fortification level was calculated using the formula:

$$\text{Fortification level} = \frac{\text{Concentration required X Sample weight}}{\text{Available concentration of the standard}}$$

3.1.9.3 Fortification of water

A 500 ml of HPLC grade water supplied by Fischer Scientific/Qualigens, Mumbai was fortified at 0.001 µg ml^{-1} and 0.0005 µg ml^{-1} by adding 50 µl and 25 µl, respectively. The extraction, cleanup procedure was followed as mentioned under section 3.1.3.

Recovery percentages were calculated using the formula

$$\text{Recovery \%} = \frac{\text{Sample area}}{\text{Standard area}} \times \frac{\text{Final volume}}{\text{Wt. of the sample}} \times \text{Standard concentration} \times \frac{100}{\text{Fortification level}}$$

3.1.10 Estimation of insecticide residues in GC-MS

The insecticide residues were estimated by injecting 1µl volume of extracted and cleaned samples in GC-MS maintained at conditions as mentioned under section 3.1.5. Based on the area of peaks obtained at the particular retention time and target and qualifier ions, which matched with those of standards, insecticide residue concentration was calculated.

Residues in Parts per million ($mg\ kg^{-1}$) =

$$\frac{\text{Sample area}}{\text{Standard area}} \times \frac{\text{Final volume}}{\text{Weight of the sample (g)}} \times \frac{\text{Vol. of std. injected}}{\text{Vol. of sample injected}} \times \text{Standard concentration (ppm)} \times \text{Recovery factor}$$

The residues obtained were compared with MRLs in particular matrix. The particulars of MRLs are given in Appendix.

3.1.11 Statistical Methods

The residue data included the following statistical calculations: means, standard deviations, relative standard deviation and linear regression analysis. Two sample t-test assuming unequal variances was conducted to compare the per cent contamination and different situations between the two villages.

3.2 EVALUATION OF IPM IN REDUCING INSECTICIDE RESIDUES

In order to assess the impact of IPM modules in the reduction of insecticide residues, samples of crop, soil and water were monitored from selected IPM farmers and the results compared with the samples collected from the non-IPM farmers from the same village or the non-contact village. As vegetables are the major source of chemical use, tomato and brinjal were covered for this study. Five tomato and five brinjal farmers were selected from Kothapally and IPM schedule was given to them. Five tomato and five brinjal farmers from Enkepally were selected as non-IPM farmers. The schedule of chemicals listed below was given on need basis in connection with pest population build up. The sample collection was similar as in the case of monitoring study. The chemical sprays were advised based on the need and considering the economic thresholds.

Table 4: IPM schedule for tomato farmers

Name of the chemical	Dose	Time of application
Neem Fruit Powder Extract (NFE) prepared at ICRISAT	5 kg $acre^{-1}$	30 DAT
Helicoverpa armigera Nuclear Polyhedrosis Virus (Ha NPV) prepared at ICRISAT	250 LE ha^{-1}	40 DAT
Endosulfan 35EC (Thiodan supplied by Excel Industries Ltd.)	2 ml l^{-1}	50 DAT
NFE	5kg $acre^{-1}$	60 DAT
Cypermethrin 25 EC (Cymbush supplied by Syngenta chemicals Ltd)	1 ml l^{-1}	70 DAT
Ha NPV	250 LE ha^{-1}	80 DAT
Endosulfan	2ml l^{-1}	90 DAT

Table 5: IPM schedule for brinjal farmers

Name of the chemical	Dose	Time of application
NFE	12 kg ha^{-1}	30 DAT
Endosulfan 35 EC	2 ml l^{-1}	40 DAT
Bacillus thuringiensis (Bt) spray (Dipel-8L supplied by Sumitomo chemicals India Pvt. Ltd)	2 ml l^{-1}	50 DAT
Cypermethrin 25 EC	1 ml l^{-1}	60 DAT
NFE	12 kg ha^{-1}	70 DAT
Endosulfan 35 EC	2 ml l^{-1}	80 DAT
Bt spray	2 ml l^{-1}	90 DAT
Cypermethrin 25 EC	1 ml l^{-1}	100 DAT
NFE	12 kg ha^{-1}	110 DAT
Endosulfan 35 EC	2 ml l^{-1}	120 DAT
Bt spray	2 ml l^{-1}	130 DAT
Cypermethrin 25 EC	1 ml l^{-1}	140 DAT
NFE	12 kg ha^{-1}	150 DAT
Endosulfan 35 EC	2 ml l^{-1}	160 DAT

DAT: Days after transplanting

NFE: 12 kg of neem fruit powder was soaked in 20 l water overnight and filtered through a muslin cloth. This was further diluted with 200 l water and was sprayed for 1 ha with motor knapsack sprayer.

RESULTS

CHAPTER IV

RESULTS

The results of the present investigation on **"Status of Insecticide Residues and Impact of Integrated Pest Management"** are presented hereunder. The experiments were conducted in the field at Kothapally watershed, Rangareddy district and the laboratory tests were taken up at the International Crops Research Institute for Semi-Arid Tropics (ICRISAT), Patancheru, Andhra Pradesh, India, during 2007-09.

4.1 MONITORING INSECTICIDE RESIDUES IN VARIOUS CROPS AND MATRICES

4.1.1 Monitoring Insecticide Residues in Food Crops, Cotton, Soil and Water from Kothapally (IPM) and Enkepally (Non-IPM) Villages during 2008 and 2009

The grain samples of rice, maize, pigeonpea, cotton lint, soil and water samples collected at the time of harvest from respective fields were analysed for the presence of two organophosphates (monocrotophos and chlorpyriphos), one organochlorine (alpha endosulfan and beta endosulfan) and synthetic pyrethroids (sum of four isomers of cypermethrin) during 2008 and 2009 from Kothapally and Enkepally. The data (Table 6) showed that out of all the grain samples analysed, one rice grain sample collected from Kothapally was contaminated with beta endosulfan (0.5 $\mu g\ g^{-1}$). Among the soil samples, alpha (0.02 $\mu g\ g^{-1}$) and beta

Table 6: Number of samples contaminated and range of insecticide residues (μg g^{-1} or μg ml^{-1}) in food crops, cotton (including soil and water) from Kothapally and Enkepally during 2008

Crop	Village	Different sample matrices with insecticide residues in μg g^{-1}														
		Grain[a]					Soil[b]					Water[c]				
		1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
Rice	Kothapally*	ND	ND	ND	1 (0.5)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Enkepally*	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Maize	Kothapally*	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Enkepally*	ND	ND	ND	ND	ND	ND	ND	1 (0.02)	1 (0.02)	ND	ND	ND	ND	ND	ND
Pigeonpea	Kothapally*	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Enkepally*	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Cotton	Kothapally*	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Enkepally*	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

*- No. of farmers (5), a-No. of grain samples analysed (5), b- No. of soil samples analysed (5), c- No. of water samples analysed (5)

1-Monocrotophos, 2-Chlorpyriphos, 3-Alpha endosulfan, 4-Beta endosulfan, 5-Cypermethrin

ND-Not detectable

Table 7: Number of samples contaminated and range of insecticide residues (µg g^{-1}) in food crops, cotton, soil and water from Kothapally and Enkepally during 2009

Crop	Village	Different sample matrices with insecticide residues in µg g^{-1}														
		Grain[a]					**Soil[b]**					**Water[c]**				
		1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
Rice	Kothapally*	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Enkepally*	ND	ND	ND	1 (0.008)	ND	ND	ND	ND	1 (0.03)	ND	ND	ND	ND	ND	ND
Maize	Kothapally*	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Enkepally*	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Pigeonpea	Kothapally*	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Enkepally*	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Cotton	Kothapally*	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Enkepally*	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

*- No. of farmers (5), a-No. of grain samples (5), b- No. of soil samples (5), c- No. of water samples (5)

1-Monocrotophos, 2-Chlorpyriphos, 3-Alpha endosulfan, 4-Beta endosulfan, 5-Cypermethrin

ND-Not detectable

endosulfan (0.02 μg g^{-1}) residues were detected in one soil sample collected from maize field in Enkepally. Only two samples contained beta endosulfan residue--one rice grain sample (0.008 μg g^{-1}) and one soil sample collected from rice field (0.03 μg g^{-1}) (Table 7) during the 2009 season from Enkepally. However, none of the pigeonpea grain, cotton lint and water samples were contaminated with insecticide residues.

4.1.2 Monitoring Insecticide Residues in Tomato Fruit, Soil and Water Collected from Kothapally and Enkepally during Different Seasons in 2008 and 2009

4.1.2.1 Monitoring insecticide residues in tomato fruits collected from Kothapally and Enkepally during different seasons in 2008 and 2009

The results of insecticide residue analysis in tomato fruit samples collected at monthly intervals and analysed for four insecticides: monocrotophos, chlorpyriphos, alpha endosulfan, beta endosulfan and cypermethrin during different cropping seasons in 2008 and 2009 from Kothapally and Enkepally are presented in tables 8 and 9.

Out of the 9 tomato fruit samples analysed during 2008 summer season from Kothapally, four (44%) samples were found to be contaminated with all the insecticide groups under study, except for chlropyriphos. Out of the four contaminated samples, the frequency of insecticide presence was twice with monocrotophos, beta endosulfan and cypermethrin and only once with alpha endosulfan, and the residue concentration ranged from 0.03-0.3 μg g^{-1}. Insecticide residues detected in tomato fruit samples from Enkepally ranged from

Table 8: Insecticide residues in tomato samples from Kothapally during different seasons in 2008 and 2009

Season	No. of samples		Insecticides detected	Frequencies	Residue level ($\mu g\ g^{-1}$)	MRL ($\mu g\ g^{-1}$)
	Analysed	Contaminated				
Summer, 2008	9	4	Monocrotophos	2	0.2, 0.2	0.2
			Alpha endosulfan	1	0.04	2.0
			Beta endosulfan	2	0.04, 0.03	2.0
			Cypermethrin	2	0.2, 0.04	0.5
Kharif, 2008	9	3	Beta endosulfan	2	0.03, 0.02	2.0
			Cypermethrin	2	0.08, 0.3	0.5
Rabi, 2008	9	...	...	...	...	...
Summer, 2009	9	3	Monocrotophos	2	0.01, 0.1	0.2
			Alpha endosulfan	1	0.2	2.0
			Cypermethrin	1	0.08	0.5
Kharif, 2009	9	1	Cypermethrin	1	0.5	0.5
Total	**45**	**11**				

Table 9: Insecticide residues in tomato samples from Enkepally during different seasons in 2008 and 2009

Season	No. of samples		Insecticides detected	Frequencies	Residue level ($\mu g\ g^{-1}$)	MRL ($\mu g\ g^{-1}$)
	Analysed	Contaminated				
Summer, 2008	6	4	Monocrotophos	1	0.3	0.2
			Alpha endosulfan	1	0.01	2.0
			Beta endosulfan	1	0.04	2.0
			Cypermethrin	2	0.1, 0.06	0.5
Kharif, 2008	6	3	Monocrotophos	2	0.006, 0.009	0.2
			Beta endosulfan	1	0.008	2.0
			Cypermethrin	1	0.07	0.5
Rabi, 2008	6	1	Alpha endosulfan	1	0.07	2.0
Summer, 2009	6	4	Monocrotophos	2	0.09, 0.05	0.2
			Alpha endosulfan	1	0.09	2.0
			Beta endosulfan	2	0.4, 0.03	2.0
			Cypermethrin	2	0.05, 0.08	0.5
Kharif, 2009	6	3	Monocrotophos	1	0.06	0.2
			Alpha endosulfan	1	0.06	2.0
			Cypermethrin	1	0.1	0.5
Total	**30**	**15**				

0.01 to 0.2 μg g^{-1} with a contamination of 67% and one sample contained the monocrotophos residue concentration above MRL. Among the 4 contaminated out of 6 samples analysed, monocrotophos, alpha endosulfan and beta endosulfan were each present in one sample and cypermethrin in two samples.

Among the contaminated samples from the Kothapally, monocrotophos was present at higher concentration (0.3 μg g^{-1}), followed by cypermethrin (0.2 μg g^{-1}), alpha endosulfan (0.04 μg g^{-1}) and beta endosulfan (0.04 μg g^{-1}). More or less similar results were obtained from the analysis of samples from Enkepally, following the decreasing order: monocrotophos (0.2 μg g^{-1}), cypermethrin (0.1 μg g^{-1}), beta endosulfan (0.04 μg g^{-1}) and alpha endosulfan (0.01 μg g^{-1}).

During *Kharif*, 2008 period, 33% (3 out of 9 samples) from Kothapally were contaminated with beta endosulfan (0.02-0.03 μg g^{-1}) and cypermethrin (0.08-0.3 μg g^{-1}). However, the residue levels were within the MRL. Though the frequency of contamination was the same for both the insecticides, cypermethrin was found in greater concentration (0.3 μg g^{-1}) than beta endosulfan (0.02-0.03 μg g^{-1}). Fifty per cent of tomato fruit samples from Enkepally contained insecticide residue ranging from 0.006 to 0.07 μg g^{-1}. The frequency of contamination with monocrotophos was greater (twice), followed by beta endosulfan and cypermethrin (once each).

None out of the nine tomato fruit samples collected from Kothapally and one out of six samples from Enkepally (17% contamination) contained insecticide residues. The residue concentration (0.07 μg g^{-1}) in the contaminated sample was far below the MRL during *Rabi*, 2008.

Analysis of tomato fruit samples during 2009 summer season showed low concentrations of monocrotophos (0.01-0.1 μg g^{-1}), alpha endosulfan (0.2 μg g^{-1}) and cypermethrin (0.08 μg g^{-1}) residues in 3 out of 9 samples (33%) from Kothapally. Out of the six samples from Enkepally, four (67%) were contaminated with monocrotophos (0.05-0.09 μg g^{-1}), beta endosulfan (0.03-0.4 μg g^{-1}), cypermethrin (0.05-0.08 μg g^{-1}) and alpha endosulfan (0.09 μg g^{-1}) residues, however the insecticide residue concentrations were below MRL in all the samples. The study indicated that monocrotophos was the major insecticide found in samples from both Kothapally and Enkepally. However, alpha endosulfan was found at highest concentration (0.2 μg g^{-1}) in samples from Kothapally and beta endosulfan (0.4 μg g^{-1}) in samples from Enkepally.

Only one sample (11% contamination) contained cypermethrin residue (0.5 μg g^{-1}) in the samples from Kothapally and 50% of samples from Enkepally showed contamination with monocrotophos (0.06 μg g^{-1}), alpha endosulfan (0.06 μg g^{-1}) and cypermethrin (0.1 μg g^{-1}) residues, but were within the prescribed MRLs during *Kharif*, 2009.

4.1.2.2 Insecticide residues in soil samples collected from tomato-planted fields during different seasons in 2008 and 2009

The data on the analysis of soil samples from two villages during different seasons are presented in tables 10 and 11. Out of the six soil samples analysed for insecticide residues from Kothapally, two samples (33%) contained cypermethrin residue ranging from 0.1 to 0.3 μg g^{-1} whereas one out of the four

Table 10: Insecticide residues in soil samples collected from tomato fields from Kothapally during different seasons in 2008 and 2009

Crop	Season	No. of samples		Insecticides detected	Frequencies	Residue level ($\mu g\ g^{-1}$)	MRL ($\mu g\ g^{-1}$)
		Analysed	Contaminated				
Tomato	Summer, 2008	6	2	Cypermethrin	2	0.1, 0.3	Not available
	Kharif, 2008	6	3	Beta endosulfan	3	0.02, 0.07, 0.04	Not available
	Rabi, 2008	6	1	Beta endosulfan	1	0.03	Not available
	Summer, 2009	6	1	Alpha endosulfan	1	0.05	Not available
	Kharif, 2009	6	...	...	...	...	...
Total		**30**	7				

Table 11: Insecticide residues in soil samples collected from tomato fields from Enkepally during different seasons in 2008 and 2009

Crop	Season	No. of samples		Insecticides detected	Frequencies	Residue level ($\mu g\ g^{-1}$)	MRL ($\mu g\ g^{-1}$)
		Analysed	Contaminated				
Tomato	Summer, 2008	4	1	Cypermethrin	1	0.01	Not available
	Kharif, 2008	4	2	Alpha endosulfan	2	0.05, 0.02	Not available
	Rabi, 2008	4	...	...	...	...	...
	Summer, 2009	4	2	Cypermethrin	1	0.04	Not available
				Alpha endosulfan	1	0.8	Not available
	Kharif, 2009	4	1	Beta endosulfan	1	0.2	Not available
Total		**20**	**6**				

samples (25%) from Enkepally contained cypermethrin residue (0.01 μg g^{-1}) during the 2008 summer season.

Soil samples collected during *Kharif*, 2008 contained beta endosulfan residue in three out of the six samples from the Kothapally with the residue concentration ranging from 0.02 to 0.07 μg g^{-1}. Similar trend was observed in Enkepally with 50% of the samples containing alpha endosulfan residue ranging from 0.02-0.05 μg g^{-1} during *Kharif*, 2008.

Majority of the soil samples collected during the 2008 *Rabi* season were free from residues and only one out of six soil samples from Enkepally contained beta endosulfan residue measuring 0.03 μg g^{-1}.

Beta endosulfan residue was found in one (25% contamination) of the soil samples of Kothapally and no soil samples from Enkepally had insecticide residues during the 2009 summer season.

Soil samples from Kothapally contained residues at not detectable levels and one out of four soil samples from Enkepally contained cypermethrin residue (0.07 μg g^{-1}) during the 2009 *Kharif* season.

4.1.2.3 Insecticide residues in water samples collected from tomato-planted fields during different seasons in 2008 and 2009

Analysis of water samples collected from sources (open wells and bore wells) that supply water to tomato fields showed residues at not detectable levels during different seasons in 2008 and 2009 (Tables 12 and 13).

Table 12: Insecticide residues in water samples collected from tomato fields from Kothapally during different seasons in 2008 and 2009.

Crop	Season	No. of samples		Insecticides detected	Frequencies	Residue level ($\mu g\ g^{-1}$)	MRL ($\mu g\ g^{-1}$)
		Analysed	Contaminated				
Tomato	Summer, 2008	6	...	...	...	...	...
	Kharif, 2008	6	...	...	...	...	...
	Rabi, 2008	6	...	...	...	...	...
	Summer, 2009	6	...	...	...	...	...
	Kharif, 2009	6	...	...	...	...	...
Total		**30**	...				

Table 13: Insecticide Residues in water samples collected from tomato fields from Enkepally during different seasons in 2008 and 2009

Crop	Season	No. of samples		Insecticides detected	Frequencies	Residue level ($\mu g\ g^{-1}$)	MRL ($\mu g\ g^{-1}$)
		Analysed	Contaminated	...	...	...	...
Tomato	Summer, 2008	4	...				
	Kharif, 2008	4	...	...	...	...	...
	Rabi, 2008	4	...	...	...	...	...
	Summer, 2009	4	...	...	...	...	...
	Kharif, 2009	4	...	...	...	...	...
Total		**20**	...				

4.1.2.4 Comparative evaluation of insecticide residues in tomato fruit, soil and water samples collected from Kothapally and Enkepally during various seasons in 2008 and 2009

A comparison of residue data of different matrices related to tomato was presented in table 14. The per cent contamination in tomato fruit samples from Enkepally was higher compared to that of Kothapally in all the seasons. The contamination percentages were as follows in Kothapally and Enkepally, respectively: 44% and 67% in summer, 2008; 33% and 67% in summer, 2009; 33% and 50% in *Kharif*, 2008; 11% and 50% in *Kharif*, 2009; 0% and 17% in *Rabi*, 2008.

Twenty five per cent of contaminated samples from Enkepally collected during summer, 2008 contained residues above MRL. However, a decrease in contamination per cent was observed during 2009 compared to 2008 in two villages.

A comparison of the data on per cent contamination in soil samples showed a decreasing trend in samples from Kothapally -- from 33% to 17% and 50% to 0% in the 2008 and 2009 summer and *Kharif* seasons, respectively. An increase in contamination percentage was observed from 25% to 50% in Enkepally during summer, 2008 and 2009. Two sample t-test assuming unequal variances showed that there is non-significant differences in per cent contamination in tomato fruit samples and soil samples between the two villages.

Table 14: Comparison of residue levels in tomato fruit, soil and water from Kothapally and Enkepally during different seasons in 2008 and 2009

Matrix	Season	Village	No. of samples		Per cent contamination	No. of samples	
			Analysed	Contaminated		Above MRLs	Per cent of samples above MRLs
Fruit	Summer, 2008	Kothapally	9	4	44	...	...
		Enkepally	6	4	67	1	25
	Summer, 2009	Kothapally	9	3	33	...	...
		Enkepally	6	4	67	...	...
	Kharif, 2008	Kothapally	9	3	33	...	...
		Enkepally	6	3	50	...	...
	Kharif, 2009	Kothapally	9	1	11	...	...
		Enkepally	6	3	50	...	...
	Rabi, 2008	Kothapally	9	...	...	...	...
		Enkepally	6	1	17	...	...
Soil	Summer, 2008	Kothapally	6	2	33		
		Enkepally	4	1	25		
	Summer, 2009	Kothapally	6	1	17		
		Enkepally	4	2	50		
	Kharif, 2008	Kothapally	6	3	50		
		Enkepally	4	2	50		
	Kharif, 2009	Kothapally	6	...	0		
		Enkepally	4	2	50		
	Rabi, 2008	Kothapally	6	...	0		
		Enkepally	4	...	17		
Water	Summer, 2008	Kothapally	6	...	...	...	...
		Enkepally	4	...	...	...	...
	Summer, 2009	Kothapally	6	...	...	...	...
		Enkepally	4	...	...	...	...
	Kharif, 2008	Kothapally	6	...	...	...	...
		Enkepally	4	...	...	...	...
	Kharif, 2009	Kothapally	6	...	...	...	...
		Enkepally	4	...	...	...	...
	Rabi, 2008	Kothapally	6	...	...	...	...
		Enkepally	4	...	...	...	...

t(cal)=2.13, non-significant (for comparison of per cent contamination in tomato fruit samples between two villages)
t(cal)= 1.52, non-significant (for comparison of per cent contamination in soil samples between two villages).

4.1.2.5 Frequency of insecticide residues and their concentration range (μg g^{-1}) in tomato fruit samples collected monthly in various seasons from Kothapally and Enkepally in 2008 and 2009

The insecticide residues frequency over the two years, was greater in summer with highest in April (5) followed by in June (4) and in May (2), while the total concentration of all insecticide residues was high in April (0.6 μg g^{-1}), followed by in May (0.5 μg g^{-1}) and in June (0.2 μg g^{-1}) in the Kothapally. The sequence of decreasing order of frequency levels and concentration levels in Enkepally was April ((6) 0.8 μg g^{-1})) > May ((3) 0.2 μg g^{-1}) > June ((2) 0.2 μg g^{-1}) (Tables 15 and 16).

During the *Kharif* season, more samples showed residues in July followed by August and September in two villages. Nevertheless, the concentration levels were high in September (0.5 μg g^{-1}) in Kothapally and in August (0.3 μg g^{-1}) in Enkepally.

4.1.2.6 Frequency of insecticide residues and concentration range (μg g^{-1}) in soil samples collected from tomato fields at the start and end of the crop seasons from Kothapally and Enkepally in 2008 and 2009

The results on the occurrence and concentration of insecticide residues in soil samples collected at beginning and end of the cropping seasons in various seasons during 2008 and 2009 (Tables 17 and 18) showed that samples collected during summer had higher incidence levels (3) at the starting of the season and none at the end in Kothapally, whereas the trend was opposite in Enkepally with high incidence (2) and concentration levels (0.8 μg g^{-1}) at the end of the season.

Table 15: **Frequency distribution of insecticide residues and concentration range (μg g^{-1}) in tomato fruit distributed over different months in different seasons from Kothapally in 2008 and 2009**

Season	Months	Organophosphates				Organochlorines				Synthetic pyrethroid		Cumulative frequency levels	Cumulative concentration levels
		Monocrotophos		Chlorpyriphos		Alpha endosulfan		Beta endosulfan		Cypermethrin			
		Year		Year		Year		Year		Year			
		2008	2009	2008	2009	2008	2009	2008	2009	2008	2009		
Summer	March	...	...	...	...	...		...	...	...	...	...	...
	April	...	2 (0.01-0.1)	...	...	...		1 (0.04)	...	1 (0.2)	...	4	0.6
	May	2 (0.2-0.3)	...	...	...	...		...	...	...	...	2	0.5
	June	...	...	...	...	1 (0.04)		1 (0.03)	...	1 (0.04)	1 (0.08)	4	0.2
	July	...	...	...	...	...		1 (0.03)	...	2 (0.08-0.3)	...	3	0.4
Kharif	August	...	...	...	...	...		1 (0.02)	...	...	...	1	0.02
	September	...	...	...	...	...		...	...	...	1 (0.5)	1	0.5
	October	...	...	...	...	...		...	...	...	...	...	...
	November	...	...	...	...	1 (0.07)		...	...	...	...	1	0.07
Rabi	December	...	...	...	...	...		...	...	...	...	...	...
	January	...	...	...	...	...		...	...	...	...	...	...
	February	...	...	...	...	...		...	...	...	...	...	...

Table 16: **Frequency distribution of insecticide residues and concentration range (μg g^{-1}) in tomato fruit distributed over different months in different seasons from Enkepally in 2008 and 2009**

Season	Months	Organophosphates				Organochlorines				Synthetic pyrethroid		Cumulative frequency levels	Cumulative concentration levels
		Monocrotophos		Chlorpyriphos		Alpha endosulfan		Beta endosulfan		Cypermethrin			
		Year		Year		Year		Year		Year			
		2008	2009	2008	2009	2008	2009	2008	2009	2008	2009		
Summer	March	...	...	...	...	...		...	...	...	...	...	...
	April	1 (0.2)	2 (0.05-0.09)	...	...	1 (0.01)	...	1 (0.04)	1 (0.4)	...	...	6	0.8
	May	...	...	...	...	...	...	...	1 (0.03)	...	2 (0.05-0.08)	3	0.2
	June	...	...	...	...	...	...	...	...	2 (0.06-0.1)	...	2	0.2
	July	1 (0.009)	...	...	...	...	1 (0.06)	1 (0.008)	...	1 (0.07)	...	4	0.1
Kharif	August	...	1 (0.06)	...	...	...	...	...	...	...	1 (0.2)	2	0.3
	September	...	...	...	...	...	...	...	...	...	1 (0.1)	1	0.1
	October	...	...	...	...	...	...	...	...	...	...	...	...
	November	...	...	...	...	...	...	...	...	...	...	...	...
	December	...	...	...	...	...	...	...	...	...	...	...	...
Rabi	January	...	...	...	...	...	...	...	...	...	...	...	...
	February	...	...	...	...	...	...	...	...	...	...	...	...

Table 17: **Frequency distribution of insecticide residues and concentration range (μg g^{-1}) in soils collected from tomato fields at the beginning and end of the crop seasons from Kothapally in 2008 and 2009**

Season	Time of collection	Organophosphates		Organochlorines		Synthetic pyrethroid		Cumulative frequency levels		Cumulative concentration levels			
		Monocrotophos		Chlorpyriphos		Alpha endosulfan		Beta endosulfan		Cypermethrin			
		Year		Year		Year		Year		Year			
		2008	2009	2008	2009	2008	2009	2008	2009	2008	2009		
Summer	Starting	...	...	...	...	...	1 (0.05)	...	...	2 (0.1-0.3)	...	3	0.5
	End	...	...	...	...	...	...	...	...	...	...	...	...
Kharif	Starting	...	...	...	...	...	...	1 (0.07)	...	...	...	1	0.07
	End	...	...	...	...	...	...	2 (0.02-0.04)	...	...	...	2	0.06
Rabi	Starting	...	...	...	...	...	...	...	...	...	...	...	...
	End	...	...	...	...	...	...	...	...	...	...	...	...

Table 18: **Frequency distribution of insecticide residues and concentration range (μg g^{-1}) in soils collected from tomato fields at the beginning and end of the crop seasons from Enkepally in 2008 and 2009**

Season	Time of collection	Organophosphates				Organochlorines				Synthetic pyrethroid		Cumulative frequency levels	Cumulative concentration levels
		Monocrotophos		Chlorpyriphos		Alpha endosulfan		Beta endosulfan		Cypermethrin			
		Year		Year		Year		Year		Year			
		2008	2009	2008	2009	2008	2009	2008	2009	2008	2009		
Summer	Starting	...	...	...	...	...	...	...	...	1 (0.01)	...	1	0.01
	End	...	...	...	...	...	1 (0.8)	...	...	...	1 (0.04)	2	0.8
Kharif	Starting	...	...	...	...	1 (0.05)	...	...	1 (0.2)	...	...	2	0.3
	End	...	...	...	...	1 (0.02)	...	...	...	...	...	1	0.02
Rabi	Starting	...	...	...	...	...	...	1 (0.03)	...	...	...	1	0.03
	End	...	...	...	...	...	...	...	...	...	...	...	...

During the *Kharif*, the occurrence and concentration of residues was higher in the soil samples collected at the end than at the start of the season in Kothapally. In contrast, higher frequency of residues and higher insecticide concentrations were observed at the beginning of the season in Enkepally.

The insecticide residue was detected only at the start of the *Rabi* season in Enkepally, but no residue was detected in the Kothapally.

4.1.3 Monitoring Insecticide Residues in Brinjal, Soil and Water Samples Collected from Kothapally and Enkepally during Various Seasons in 2008

4.1.3.1 Monitoring insecticide residues in brinjal collected from Kothapally and Enkepally during different seasons in 2008 and 2009

The results on the insecticide residues detected in brinjal samples and the frequency of their occurrence and concentrations in 2008 and 2009 are shown in tables 19 and 20.

During summer, 2008, the frequency of contamination was high with cypermethrin, followed by monocrotophos and beta endosulfan; and the residue concentration ranged from 0.02 to 0.1 $\mu g\ g^{-1}$ in Kothapally. All four groups of insecticides were found in the contaminated samples and the frequency of contamination was similar for all the groups of insecticides with concentrations ranging from 0.009 to 2.0 $\mu g\ g^{-1}$ in Enkepally. Cypermethrin residue was found at higher concentration (0.1 $\mu g\ g^{-1}$) in the brinjal fruit samples from Kothapally. Beta

Table 19: Insecticide residues in brinjal samples from Kothapally during different seasons in 2008 and 2009

Season	No. of samples		Insecticides detected	Frequencies	Residue level ($\mu g\ g^{-1}$)	MRL ($\mu g\ g^{-1}$)
	Analysed	Contaminated				
Summer, 2008	8	3	Monocrotophos	1	0.02	0.2
			Beta endosulfan	1	0.07	2.0
			Cypermethrin	2	0.07, 0.1	0.2
Kharif, 2008	8	5	Monocrotophos	3	0.2, 0.03, 0.01	0.2
			Cypermethrin	5	0.05, 0.05, 0.1, 0.04, 0.01	0.2
Rabi, 2008	8	2	Monocrotophos	1	0.03	0.2
			Cypermethrin	1	0.05	0.2
Summer, 2009	8	4	Monocrotophos	1	0.2	0.2
			Alpha endosulfan	1	0.01	2.0
			Cypermethrin	2	0.03, 0.2	0.2
Kharif, 2009	8	3	Alpha endosulfan	1	0.06	2.0
			Beta endosulfan	1	0.05	2.0
			Cypermethrin	2	0.1, 0.03	0.2
Total	**40**	**17**				

Table 20: Insecticide residues in brinjal samples from Enkepally during different seasons in 2008 and 2009

Season	No. of samples		Insecticides detected	Frequencies	Residue level (µg g^{-1})	MRL (µg g^{-1})
	Analysed	Contaminated				
Summer, 2008	8	6	Monocrotophos	2	0.06, 0.1	0.2
			Chlorpyriphos	1	0.009	0.2
			Alpha endosulfan	2	1.0, 0.9	2.0
			Beta endosulfan	2	1.0, 3.0	2.0
			Cypermethrin	2	0.05, 0.02	0.2
Kharif, 2008	8	6	Monocrotophos	3	0.01, 0.09, 0.006	0.2
			Alpha endosulfan	2	0.06, 0.01	2.0
			Beta endosulfan	1	0.02	2.0
			Cypermethrin	1	0.09	0.2
Rabi, 2008	8	5	Monocrotophos	2	0.09, 0.009	0.2
			Alpha endosulfan	1	0.06	2.0
			Cypermethrin	2	0.009, 0.1	0.2
Summer, 2009	8	7	Monocrotophos	2	0.01, 0.03	0.2
			Alpha endosulfan	3	0.07, 0.009, 0.01	2.0
			Beta endosulfan	2	0.006, 0.08	2.0
			Cypermethrin	1	0.02	0.2
Kharif, 2009	8	5	Monocrotophos	1	0.02	0.2
			Chlorpyriphos	1	0.01	0.2
			Alpha endosulfan	1	2.0	2.0
			Beta endosulfan	1	0.9	2.0
			Cypermethrin	3	0.2, 0.1, 0.06	0.5
Total	**40**	**29**				

endosulfan was present in greater concentration (3.0 μg g^{-1}) and above MRL among all the insecticides in the samples from Enkepally.

A contamination level of 63% with cypermethrin as the main contaminant recording a frequency of incidence as 5 times, followed by monocrotophos with 3 times incidence and the residue concentration ranged from 0.01 to 0.2 μg g^{-1}. All the insecticides analysed except for chlorpyriphos, were detected in 6 out of the 8 samples (75%) collected from Enkepally and the concentration ranged from 0.006 to 0.09 μg g^{-1}. Among the insecticides found, the incidence (3 times) and residue concentration of monocrotophos was high (0.09 μg g^{-1}) during *Kharif*, 2008.

In samples collected from Kothapally during *Rabi*, 2008, the residues of monocrotophos and cypermethrin were detected (0.03 to 0.05 μg g^{-1}) (25% samples were contaminated). In Enkepally, 5 out of 8 samples had insecticide residues with most containing monocrotophos and cypermethrin residues, followed by alpha endosulfan (0.009 to 0.1 μg g^{-1}).

Fifty per cent of the samples were contaminated in Kothapally during 2009 summer season. The incidence and the concentration followed the order: cypermethrin > monocrotophos > alpha endosulfan (0.01 to 0.2 μg g^{-1}) in samples collected from Kothapally. In contrast, all the insecticides analysed, except for chlorpyriphos were present (0.006-0.08 μg g^{-1}) in 88% of the samples collected from Enkepally. Although alpha endosulfan was the major contaminant, beta endosulfan concentration was found to be greater (0.08 μg g^{-1}).

Organochlorine insecticides *viz.*, alpha endosulfan and beta endosulfan (0.05 to 0.06 μg g^{-1}) and cypermethrin (0.03 to 0.1 μg g^{-1}) were detected in 3 out of 8 (58%) samples collected from the Kothapally. However, all the insecticides analysed were found (0.01 to 2.0 μg g^{-1}) in 5 out of 8 samples (63%) collected from Enkepally during the 2009 *Kharif* season.

4.1.3.2 Insecticide residues in soil samples collected from fields with brinjal crop during different seasons in 2008 and 2009

The data on the insecticide residues in soil samples collected during 2008 and 2009 are given in tables 21 and 22. Twenty five per cent of the samples collected from the two villages contained residues. Monocrotophos (0.06 μg g^{-1}) and chlorpyriphos (0.03 μg g^{-1}) were detected in the samples from Kothapally and Enkepally, respectively in 2008 summer season.

During the 2008 *Kharif* season, insecticide residues were not detected in the samples collected from Kothapally and Enkepally.

No detectable amount of residues was present in soil and water samples from the Kothapally, while one out of the four samples (25%) collected from Enkepally contained the residues of alpha endosulfan and cypermethrin (0.02 to 0.1 μg g^{-1}) during the 2008 *Rabi* season.

During the 2008 summer season, beta endosulfan (0.01 μg g^{-1}) was present in one out of 4 samples (25%) from Kothapally and none of the samples from Enkepally contained insecticide residues.

Table 21: Insecticide residues in soil samples collected from brinjal fields from Kothapally during different seasons in 2008 and 2009

Crop	Season	No. of samples		Insecticides detected	Frequencies	Residue level ($\mu g\ g^{-1}$)	MRL ($\mu g\ g^{-1}$)
		Analysed	Contaminated				
Brinjal	Summer, 2008	4	1	Monocrotophos	1	0.06	Not available
	Kharif, 2008	4	...	...	...	...	...
	Rabi, 2008	4	...	...	...	...	...
	Summer, 2009	4	1	Beta endosulfan	1	0.01	Not available
	Kharif, 2009	4	...	...	...	...	...
Total		**20**	**2**				

Table 22: Insecticide residues in soil samples collected from brinjal fields from Enkepally during different seasons in 2008 and 2009

Crop	Season	No. of samples		Insecticides detected	Frequencies	Residue level ($\mu g\ g^{-1}$)	MRL ($\mu g\ g^{-1}$)
		Analysed	Contaminated				
Brinjal	Summer, 2008	4	1	Chlorpyriphos	1	0.03	Not available
	Kharif, 2008	4	...	...	...	...	...
	Rabi, 2008	4	1	Alpha endosulfan	1	0.1	Not available
				Cypermethrin	1	0.02	Not available
	Summer, 2009	4	...	...	...	...	...
	Kharif, 2009	4	1	Cypermethrin	1	0.07	Not available
Total		20	3				

Table 23: Insecticide residues in water samples collected from brinjal fields from Kothapally during different seasons in 2008 and 2009

Crop	Season	No. of samples		Insecticides detected	Frequencies	Residue level ($\mu g\ g^{-1}$)	MRL ($\mu g\ g^{-1}$)
		Analysed	Contaminated				
Brinjal	Summer, 2008	4	...	...	...	...	...
	Kharif, 2008	4	...	...	...	...	...
	Rabi, 2008	4	...	...	...	...	...
	Summer, 2009	4	...	...	...	...	...
	Kharif, 2009	4	...	...	...	...	...
Total		20	...				

Table 24: Insecticide residues in water samples collected from brinjal fields from Enkepally during different seasons in 2008 and 2009

Crop	Season	No. of samples		Insecticides detected	Frequencies	Residue level ($\mu g\ g^{-1}$)	MRL ($\mu g\ g^{-1}$)
		Analysed	Contaminated	...	...	...	...
Brinjal	Summer, 2008	4	...	...	...	...	...
	Kharif, 2008	4	...	...	...	...	...
	Rabi, 2008	4	...	...	...	...	...
	Summer, 2009	4	...	...	...	...	...
	Kharif, 2009	4	...	...	...	...	...
Total		20	...				

4.1.3.3 Insecticide residues in water samples collected from brinjal fields during different seasons in 2008 and 2009

Water samples from the two villages contained undetectable amount of residues in all the seasons (Table 23 and 24).

4.1.3.4 Comparative evaluation of insecticide residues in brinjal fruit, soil samples collected from Kothapally and Enkepally in various seasons during 2008 and 2009

The comparison of insecticide residues in various matrices relative to the brinjal is summarized in table 25. The per cent contamination of fruit samples was lower in samples collected from the Kothapally than in those from Enkepally in all the seasons. The contamination percentages were as follows in Kothapally and Enkepally, respectively: 58% and 75% in summer, 2008; 50% and 88% in summer, 2009; 63% and 75% in *Kharif*, 2008; 58% and 63% in *Kharif*, 2009; 25% and 63% in *Rabi*, 2008. Seventeen per cent and 20% of the samples contained residue above the MRLs in Enkepally during summer, 2008 and *Kharif*, 2009, respectively.

The soil sample analysis indicated same contamination level (25%) in the two villages during summer, 2008. The per cent contamination was high in Enkepally samples during *Kharif*, 2009 and *Rabi*, 2008. Two sample t-test assuming unequal variances showed that there is significant difference in per cent contamination in brinjal samples and non-significant difference in soil samples between the two villages.

Table 25: Comparison of residue levels in brinjal fruit, soil and water from Kothapally and Enkepally during various seasons in 2008 and 2009

Matrix	Season	Village	No. of samples		Per cent contamination	No. of samples	
			Analysed	Contaminated		Above MRLs	Per cent of samples above MRLs
Fruit	Summer, 2008	Kothapally	8	3	58	...	...
		Enkepally	8	6	75	1	17
	Summer, 2009	Kothapally	8	4	50	...	...
		Enkepally	8	7	88	...	...
	Kharif, 2008	Kothapally	8	5	63	...	...
		Enkepally	8	6	75	...	...
	Kharif, 2009	Kothapally	8	3	58	...	...
		Enkepally	8	5	63	1	20
	Rabi, 2008	Kothapally	8	2	25	...	...
		Enkepally	8	5	63	...	...
Soil	Summer, 2008	Kothapally	4	1	25	...	...
		Enkepally	4	1	25	...	...
	Summer, 2009	Kothapally	4	1	25	...	...
		Enkepally	4	...	0	...	...
	Kharif, 2008	Kothapally	4	...	0	...	...
		Enkepally	4	...	0	...	...
	Kharif, 2009	Kothapally	4	...	0	...	...
		Enkepally	4	1	25	...	...
	Rabi, 2008	Kothapally	4	...	0	...	...
		Enkepally	4	1	25	...	...
Water	Summer, 2008	Kothapally	6	...	...	...	...
		Enkepally	4	...	...	...	...
	Summer, 2009	Kothapally	6	...	...	...	...
		Enkepally	4	...	...	...	...
	Kharif, 2008	Kothapally	6	...	...	...	...
		Enkepally	4	...	...	...	...
	Kharif, 2009	Kothapally	6	...	...	...	...
		Enkepally	4	...	...	...	...
	Rabi, 2008	Kothapally	6	...	...	...	...
		Enkepally	4	...	...	...	...

t (cal)= 2.67, significant (for comparison of per cent contamination in brinjal fruit samples between two villages)

t (cal)= 0.57, non-significant (for comparison of per cent contamination in soil samples between two villages).

4.1.3.5 Frequency distribution of insecticide residues and their concentration range (μg g^{-1}) in brinjal fruit samples collected monthly in various seasons during 2008 and 2009 from Kothapally and Enkepally

The results of cumulative frequency levels and concentration ranges of insecticide residues in brinjal fruit during different months in different seasons over a two year period (2008 and 2009) are given in Tables 26 and 27.

During the summer season, greater level of insecticide residues was observed in May (4), followed by March (2) and April (2), but the concentration was less in May (0.2 μg g^{-1}) and similar in March and April (0.3 μg g^{-1}) in samples from Kothapally. A decreasing order in the frequency levels in Enkepally was: March (7) > May (5) > April (3) > June (2) while the order in insecticide concentration was: May (2.2 μg g^{-1}) > March (2.1 μg g^{-1}) > June (1.0 μg g^{-1}) > April (0.06 μg g^{-1}).

The concentration and distribution of insecticide residues during the *Kharif* followed the order: July ((5) 0.4 μg g^{-1}) > August ((5) 0.2 μg g^{-1}) > September ((2) 0.2 μg g^{-1}) > October (0) in Kothapally. The frequency of the distribution of insecticide residues in Enkepally followed the order: July (7) > September (3) > August (2) > October (2); while higher concentrations were found in September (2.1 μg g^{-1}), followed by in August (1.0 μg g^{-1}), July (0.4 μg g^{-1}) and October (0.1 μg g^{-1}).

During *Rabi*, the residue levels were same in November (1) and December (1), but the residue concentration was greater in December (0.05 μg g^{-1}) in

Table 26: **Frequency distribution of insecticide residues and concentration range (µg g^{-1}) in brinjal fruit distributed over different months in different seasons from Kothapally in 2008 and 2009.**

Season	Months	Organophosphates				Organochlorines				Synthetic pyrethroid		Cumulative frequency levels	Cumulative concentration levels
		Monocrotophos		Chlorpyriphos		Alpha endosulfan		Beta endosulfan		Cypermethrin			
		Year		Year		Year		Year		Year			
		2008	2009	2008	2009	2008	2009	2008	2009	2008	2009		
	March	...	...	...	...	...	...	...	...	1 (0.1)	1 (0.2)	2	0.3
Summer	April	...	1 (0.2)	...	...	...	...	...	...	1 (0.07)	...	2	0.3
	May	1 (0.02)	...	...	...	...	1 (0.01)	1 (0.07)	...	...	1 (0.03)	4	0.2
	June	...	...	...	...	...	...	...	...	...	...	...	...
	July	2 (0.01-0.2)	...	...	...	...	...	...	...	2 (0.04-0.05)	1 (0.1)	5	0.4
Kharif	August	1 (0.03)	...	...	...	...	...	...	1 (0.05)	2 (0.01-0.05)	1 (0.03)	5	1.0
	September	...	...	...	...	...	1 (0.06)	...	...	1 (0.1)	...	2	2.1
	October	...	...	...	...	...	...	...	...	...	...	...	0.1
	November	1 (0.03)		...	...	...	...	...	...	...	...	1	0.03
Rabi	December	...	...	...	...	...	...	...	...	1 (0.05)	...	1	0.05
	January	...	...	...	...	...	...	...	...	...	...	...	...
	February	...	...	...	...	...	...	...	...	...	...	...	...

Table 27: Frequency distribution of insecticide residues and concentration range (μg g^{-1}) in brinjal fruit distributed over different months in different seasons from Enkepally in 2008 and 2009

Season	Months	Organophosphates				Organochlorines				Synthetic pyrethroid		Cumulative frequency levels	Cumulative concentration levels
		Monocrotophos		Chlorpyriphos		Alpha endosulfan		Beta endosulfan		Cypermethrin			
		Year		Year		Year		Year		Year			
		2008	2009	2008	2009	2008	2009	2008	2009	2008	2009		
Summer	March	1 (0.06)	1 (0.03)	...	...	1 (1.0)	...	1 (1.0)	1 (0.006)	1 (0.02)	1 (0.02)	7	2.1
	April	...	1 (0.01)	...	...	...	1 (0.009)	...	...	1 (0.05)	...	3	0.06
	May	1 (0.1)	...	1 (0.009)	...	...	2 (0.01-0.07)	1 (2.0)	...	...	...	5	2.2
	June	...	...	...	...	1 (0.9)	...	...	1 (0.08)	...	...	2	1.0
Kharif	July	2 (0.006-0.01)	1 (0.02)	...	1 (0.01)	1 (0.06)	...	...	...	...	2 (0.1-0.2)	7	0.4
	August	1 (0.09)	...	...	...	...	...	...	1 (0.9)	...	...	2	1.0
	September	...	...	...	...	1 (0.01)	1 (2.0)	...	...	...	1 (0.06)	3	2.07
	October	...	...	...	...	...	...	1 (0.02)	...	1 (0.09)	...	2	0.1
	November	2 (0.009-0.09)	...	...	...	...	...	...	...	...	...	2	0.1
Rabi	December	...	...	...	...	1 (0.06)	...	...	...	1 (0.1)	...	2	0.2
	January	...	...	...	...	...	...	...	...	1 (0.009)	...	1	0.009
	February	1 (0.009)	...	...	...	...	...	...	...	...	...	1	0.009

the samples from the Kothapally. Similar results with respect to incidence and concentration levels was also observed in Enkepally.

4.1.3.6 Frequency of insecticide residues and concentration range (μg g^{-1}) in soil samples collected at the start and end of the cropping from brinjal fields in Kothapally and Enkepally during 2008 and 2009 seasons

The frequency and concentration of insecticide residues found in soil samples collected at the start and end of the crop season from brinjal fields are given in tables 28 and 29.

The insecticide residue was detected only at the end of the cropping season in summer in Kothapally and the reverse was the case in Enkepally and the residue was detected only at the start of the season.

The soil samples collected during the *Kharif* season from the two villages showed no residues at the start or end of the season. During the *Rabi* season, none of the soil samples from the Kothapally contained insecticide residues. However, the insecticide residues were detected at the start of the season in samples from Enkepally.

4.1.3.7 Overall per cent contamination in different matrices in 2008 and 2009

Out of the total 45 tomato fruit samples from Kothapally analysed for insecticide residues over a period of five seasons in 2008 and 2009, 11 samples were found to contain residues (27%). The residue concentration was found in 47% (14 out of 30 samples were contaminated) of the samples collected from Enkepally during the same period.

Table 28: **Frequency distribution of insecticide residues and concentration range (μg g^{-1}) in soils collected from brinjal fields at the beginning and end of the crop seasons from Kothapally in 2008 and 2009**

Season	Time of collection	Organophosphates				Organochlorines				Synthetic pyrethroid		Cumulative frequency levels	Cumulative concentration levels
		Monocrotophos		Chlorpyriphos		Alpha endosulfan		Beta endosulfan		Cypermethrin			
		Year		Year		Year		Year		Year			
		2008	2009	2008	2009	2008	2009	2008	2009	2008	2009		
	Starting	...	...	...	...	...	...	...	...	...	...	...	...
Summer	End	1 (0.06)	...	...	...	...	...	...	1 (0.01)	...	...	2	0.07
Kharif	Starting	...	...	...	...	...	...	...	...	...	...	...	...
	End	...	...	...	...	...	...	...	...	...	...	...	...
Rabi	Starting	...	...	...	...	...	...	...	...	...	...	...	...
	End	...	...	...	...	...	...	...	...	...	...	...	...

Table 29: Frequency distribution of insecticide residues and concentration range (µg g^{-1}) in soils collected from brinjal fields at the beginning and end of the crop seasons from Enkepally in 2008 and 2009

Season	Time of collection	Organophosphates				Organochlorines				Synthetic pyrethroid		Cumulative frequency levels	Cumulative concentration levels
		Monocrotophos		Chlorpyriphos		Alpha endosulfan		Beta endosulfan		Cypermethrin			
		Year		Year		Year		Year		Year			
		2008	2009	2008	2009	2008	2009	2008	2009	2008	2009		
Summer	Starting	…	…	1 (0.03)	…	…	…	…	…	…	…	1	0.03
	End	…	…	…	…	…	…	…	…	…	…	…	…
Kharif	Starting	…	…	…	…	…	…	…	…	…	…	…	…
	End	…	…	…	…	…	…	…	…	…	…	…	…
Rabi	Starting	…	…	…	…	1 (0.1)	…	…	…	1 (0.02)	…	2	0.12
	End	…	…	…	…	…	…	…	…	…	…	…	…

Out of the 30 soil samples collected from tomato fields, only six samples contained insecticide residues (24%). Out of the 20 soil samples analysed from Enkepally, 5 were contaminated with contamination percentage of 35.

Among the 40 brinjal fruit samples analysed during 2008-2009 seasons, 17 (43%) samples from Kothapally and 29 (73%) samples from Enkepally contained insecticide residues.

Only 10% and 15% of the soil samples collected from brinjal fields were contaminated in Kothapally and Enkepally, respectively (Tables 30 and 31).

4.1.4 Farmers' perception on plant protection in Kothapally (contact village) and Enkepally (Non-contact village)

A survey was conducted to know from the farmers about their views on the present-day plant protection practices followed in various crop production systems. The salient findings from the survey are presented below:

The interactive sessions with farmers in the two villages indicated that the size of land holdings ranged from 1.5 to 20 acres in the Kothapally and from 2 to 20 acres in Enkepally. The survey covered farmers with farming experience ranging from 1 to 40 in the contact (Kothapally) and from 3 to 45 years in the non-contact village (Enkepally) (Table 32).

4.1.4.1 Farmers' plant protection practices and the sources of information

The present study brought out that most of the farmers (80-86%) initiate the plant protection practices based on the first appearance of the pest in both the

Table 30: Overall per cent contamination of tomato, brinjal, food crops, cotton, soil and water samples with insecticide residues from Kothapally during the period of study (2008, 2009)

Matrix	No. of samples		Per cent contamination	Percent of samples above MRLs
	Analysed	Contaminated		
Vegetables				
Tomato	45	11	24	--
Brinjal	40	17	43	--
Total	**85**	**28**	**33**	--
Food crops				
Rice	10	1	10	--
Maize	10	0	0	---
Pigeonpea	10	0	0	--
Cotton	10	0	0	--
Total	**40**	**1**	**2.5**	--
Soil from different fields				
Vegetables				--
Tomato	30	6	20	--
Brinjal	20	2	10	--
Total	**50**	**8**	**16**	--
Food crops				
Rice	10	0	0	--
Maize	10	0	0	--
Pigeonpea	10	0	0	--
Cotton	10	0	0	--
Total	**40**	**0**	**0**	--
Water	80	0	0	-

Table 31: Over all per cent contamination of tomato, brinjal, food crops, cotton, soil and water samples with insecticide residues from Enkepally during the period of study (2008, 2009)

Matrix	No. of samples		Per cent contamination	Percent of samples above MRLs
	Analysed	Contaminated		
Vegetables				
Tomato	30	15	50	7
Brinjal	40	29	73	7
Total	**70**	**44**	**63**	--
Food crops and cotton				
Rice	10	1	10	--
Maize	10	...	0	--
Pigeonpea	10	...	0	--
Cotton	10	...	0	--
Total	**40**	**1**	**2.5**	--
Soil from different fields				
Vegetables				
Tomato	20	7	35	--
Brinjal	20	3	15	--
Total	**40**	**10**	**25**	--
Food crops and cotton				
Rice	10	1	10	--
Maize	10	...	...	--
Pigeonpea	10	...	...	--
Cotton	10	...	...	--
Total	**40**	**1**	**2.5**	--
Water	70	...	0	--

Table 32: Gender, land holding and farming experience of farmers in Kothapally and Enkepally

S. No.	Kothapally				Enkepally			
	Farmer's name	Gender	Land holding (Acres)	Farming experience (Years)	Farmer's name	Gender	Land holding	Farming experience
1	T. Venkataiah	Male	12	10	B. Buchi Reddy	Male	20	20
2	P. Narasimha Reddy	Male	18	40	B. Venkat Reddy	Male	10	20
3	Md. Yusuf	Male	5	8	B.Venkataiah	Male	3	10
4	C. Balaiah	Male	1.5	45	T. Yadaiah	Male	5	20
5	P. Mahipal Reddy	Male	12	20	Y. Aadi Reddy	Male	4	3
6	K. Narayana Reddy	Male	12	40	P. Raji Reddy	Male	12	20
7	B. Balaram Reddy	Male	9	20	P. Laxma Reddy	Male	3	20
8	V. Paramaiah	Male	2	35	S.Sudharshan Reddy	Male	4	25
9	A. Sattaiah	Male	4	20	S. Narayana Reddy	Male	5	20
10	V. Mallaiah	Male	5	30	S. Vittal Reddy	Male	6	45
11	P. Padamakar	Male	3	4	S. Pratap Reddy	Male	6	10
12	O. Narasimha	Male	8	40	K. Anjaiah	Male	4	20
13	S. Yellaiah	Male	7	15	S. Mohana Reddy	Male	12	7
14	M. Govardhan	Male	3	10	T. Shekar Goud	Male	3	10
15	K. Prabhu	Male	3	15	K. Ravindra	Male	15	18
16	M. Narahari	Male	4	20	Ch.Krishnayya	Male	4	45
17	K. Sambaiah Goud	Male	10	15	P. Neel Reddy	Male	6	20
18	D. Ananthaiah	Male	8	30	Ch. Yadaiah	Male	2	20
19	B. Mahipal Reddy	Male	7	12	Y. Laxma Reddy	Male	15	35
20	V.Ramachandraiah	Male	3	30	Ch.Anjaneyulu	Male	3	10
21	S. Rajendra Reddy	Male	12	15	K. Laxman Goud	Male	4	15
22	K. Raju	Male	4	1	K. Krishna	Male	10	27
23	V. Jangaiah	Male	20	18	S. Manikya Reddy	Male	14	7
24	P. Narasimhulu	Male	9	15	P. Narasimha Reddy	Male	4	12
25	A. Balwanth Reddy	Male	20	10	S. Anji Reddy	Male	4	6

villages irrespective of their population, crop stage and the damage caused. Only 8% and 4% farmers followed the economic threshold concept by monitoring the pest population based on the crop stage and the economic impact and 4% and 12% of the farmers followed neighbourers; and 4% and 8% of the farmers followed the calendar-based plant protection practices in Kothapally and Enkepally, respectively (Table 33, Graph1).There is no significant difference between the two villages in respect of plant protection practices.

4.1.4.2 Sources of plant protection advice to farmers

Thirty eight per cent of the farmers in Kothapally and 50% in Enkepally got their plant protection advice from pesticide dealers. Thirty five per cent and 20% of the farmers implemented plant protection according to the advice from the agricultural officers; Ten per cent and 17% followed the advice from neighbourers in the Kothapally and Enkepally, respectively. In Kothapally, 17% of the farmers made the plant protection decision based on their own observations, while in Enkepally 13% of the farmers fell in this group (Table 34, Graph 2).

4.1.4.3 Farmer's confidence in the use of chemicals

Though 100% of the farmers used chemical pesticides for pest control, a majority (88%) of them felt that they were not working effectively. Unknown reasons were assigned for the failure of pest control by 12% and 20% of farmers from Kothapally and Enkepally, respectively. Fourty per cent of the farmers from Kothapally and 32% from Enkepally indicated that the poor efficacy was due to the presence of spurious/duplicate pesticides in the market; and 14% (Kothapally) and 8% (Enkepally) of the farmers in these two villages felt that the poor efficacy was

Table 33: Sources of plant protection practices followed by farmers in Kothapally and Enkepally

Events of initiation	Initiation conditions	
	Kothapally	Enkepally
At the appearance of pest	86	80
Economic threshold	8	4
Neighbours	4	8
Calendar basis	2	8

t (cal)=0, non-significant

Table 34: Sources of plant protection advice to farmers in Kothapally and Enkepally

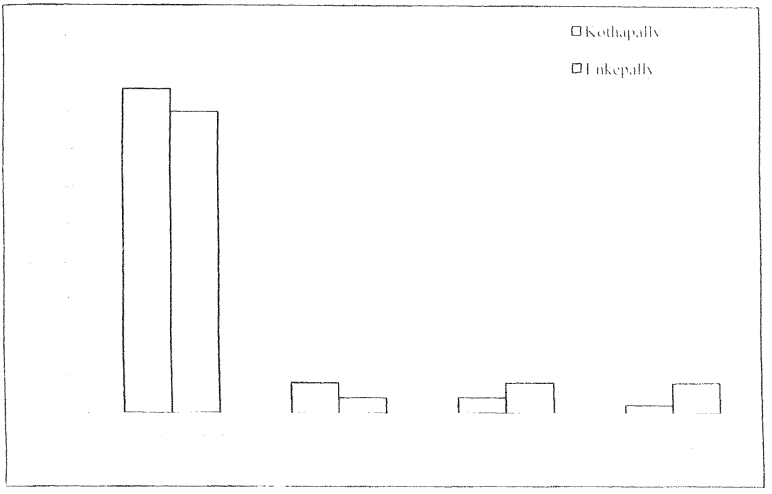
Sources	Advice (%)	
	Kothapally	Enkepally
Pesticide dealer	38	50
Agricultural officer	35	20
Neighbours	10	17
Own judgement	17	13

t (cal)=0, non-significant

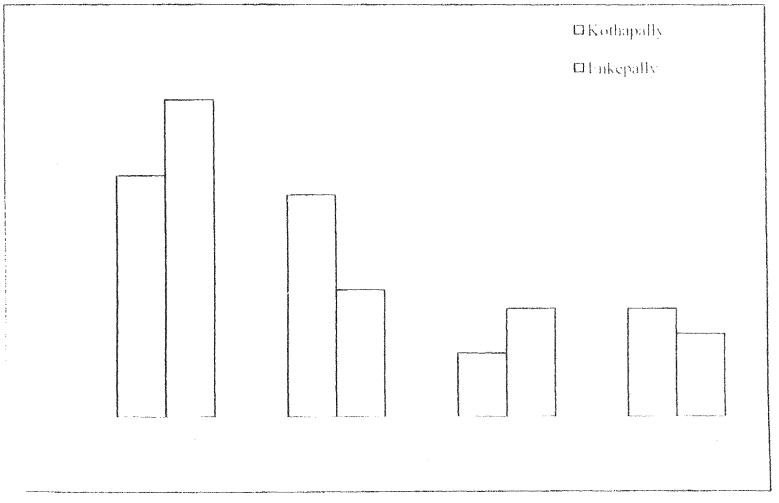
Table 35: Reasons assigned by farmers for failure or poor efficacy of pest control practices in Kothapally and Enkepally

Reasons	Belief (%)	
	Kothapally	Enkepally
Unknown reasons	12	20
Low power	34	40
Duplicate pesticides	40	32
Resistance development	14	8

t (cal)=0, non-significant



Graph 1: Initiation of plant protection practices in Kothapally and Enkepally



Graph 2: Sources of plant protection advice to farmers in Kothapaly and Enkepally

due to the development of resistance in pests to the chemicals used (Table 35; Graph 3).

4.1.4.4 Awareness about the effects of pest control measures on health

The surveys indicated that most of the farmers in Kothapally and Enkepally expressed health problems due to the use of chemicals used for plant protection. However, only 32% of the farmers in Kothapally and 12% in Enkepally used protective clothing while applying the toxic plant protection chemicals. Amongst the various health problems, 22% of farmers complained of skin rashes, 12% of nausea, 32% of headache, 26% of irritation in the eyes and 8% of dizziness associated with the sprays of plant protection chemicals. A similar opinion was also expressed by farmers in Enkepally (Skin rash-24%, nausea-18%, headache-36%, eye irritation-20% and dizziness-2%) (Table 36).

4.1.4.5 Awareness about the chemical/pesticide residues and safe waiting period to avoid pesticide residues

Fourty four per cent of the farmers in Kothapally were aware of the residual effects of pesticides, while only 16% of the farmers in Enkepally knew about the pesticide residues. Around 30% of the farmers followed a waiting period of one week in both the villages. A waiting period of 2-5 days was followed by 60% and 45% of farmers from Kothapally and Enkepally, respectively. Only 10-25% of the farmers adopted only one day waiting period from the two villages (Table 37, Graph 4).

Table 36: Farmer's awareness about health problems due to pesticides and use of protective clothing in Kothapally and Enkepally.

Health problems and protective clothing	Per cent	
	Kothapally	Enkepally
Skin rash	22	24
Nausea	12	18
Head ache	32	36
Eye irritation	26	20
Dizziness	8	2
Protective clothing	32	12

t (cal)=0.53, non-significant

Table 37: Awareness on pesticide residues and safe waiting period followed by farmers in Kothapally and Enkepally

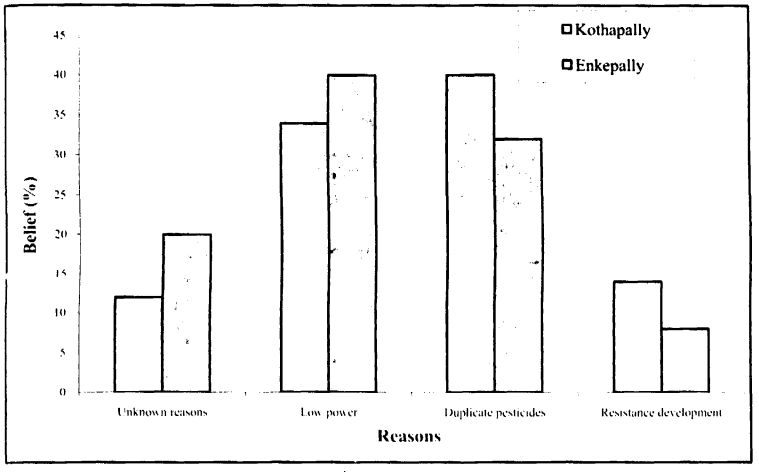
	Awareness %	
	Kothapally	Enkepally
Awareness on pesticide residues	44	16
Safe waiting period %		
1 week	30	30
2-5 days	60	45
1 day	10	25

t (cal)=0.57, non-significant

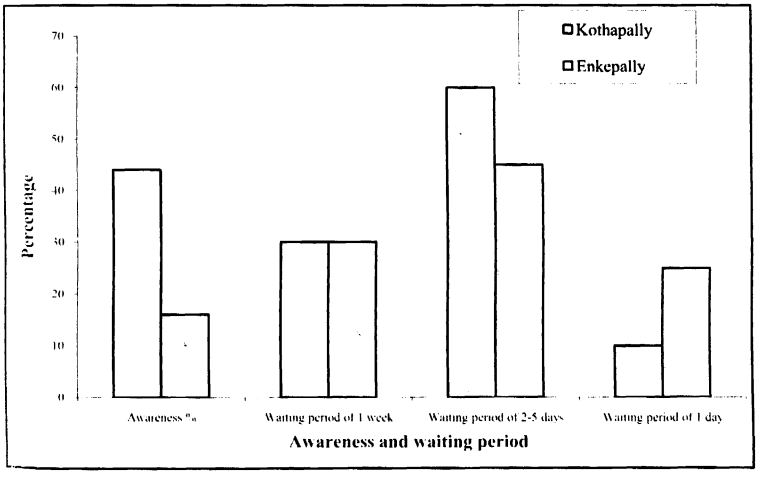
Table 38: Farmers knowledge on Integrated Pest Management in Kothapally and Enkepally

Awareness	Knowledge %	
	Kothapally	Enkepally
Awareness of IPM	48	16
Biopesticides	36	25
Cultural methods	36	56
Natural enemies	28	19

t (cal)=0.79, non-significant



Graph 3: Reasons assigned by farmers for the failure or poor efficacy of the pest control practices in Kothapally and Enkepally



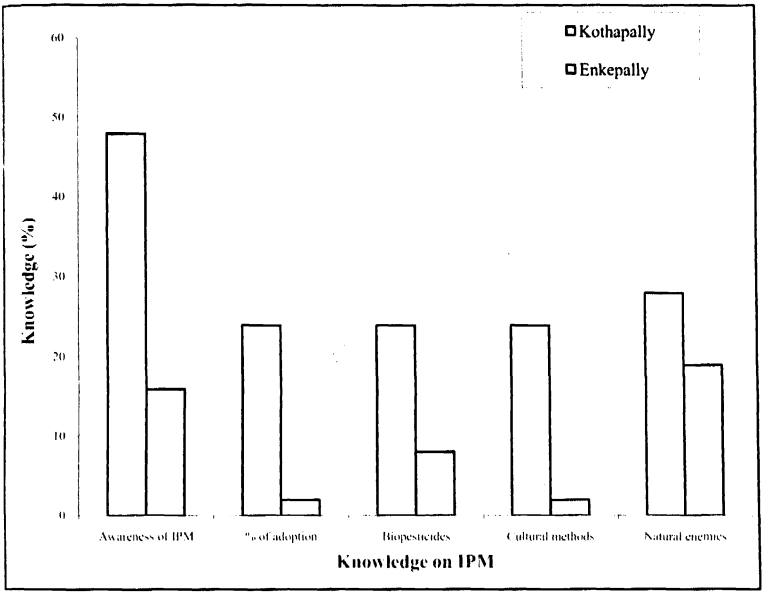
Graph 4: Awareness on pesticide residues and safe waiting period followed by farmers in Kothapally and Enkepally

4.1.4.6 Farmers' knowledge on the Integrated Pest Management (IPM)

Though IPM has been advocated for the past few years in the contact village, only 48% of farmers in Kothapally and 16% in Enkepally were aware of the IPM. Although 48% of farmers in Kothapally were aware of IPM, only half of them adopted it. The percentage of farmers who used biopesticides (Neem/NPV) were 26% and 25% in contact and non-contact villages, respectively. Thirty six per cent followed cultural methods (use of intercrops and trap crops, bird perches, shaking of infested plants) in Kothapally and 56% in Enkepally. Twenty eight per cent and 19% had the knowledge of natural enemies in Kothapally and Enkepally, respectively (Table 38, Graph 5).

4.1.4.7 Chemical usage on different crops

Survey brought out the following average number of sprays on various crops: traditional cotton (20, 21 numbers), Bt cotton (3, 4), paddy (3, 4), maize (no sprays usually but occasionally phorate granules were applied during the initial stages of the crop), pigeonpea (2, 3), chickpea (3, 2), tomato (7, 9), brinjal (12, 15), okra (13, 20), chilli (3, 4), cabbage (4, 8), cucumber (2, 2), onion (2, 4), kheera (2, 3), leafy vegetable (2, 8), marigold (3, 3) in Kothapally and Enkepally, respectively. Of these, cotton was found to be highly sprayed crop with 20-21 sprays, followed by vegetables. Among the vegetables, okra received more insecticide sprays, followed by brinjal, tomato, cabbage and leafy vegetables (Table 39). However, traditional cotton has been replaced by Bt cotton in both the villages to a great extent.



Graph 5: Farmers knowledge on IPM in Kothapally and Enkepally

Table 39: Number of insecticide sprays on different crops in Kothapally and Enkepally

Crop	Kothapally	Enkepally
Traditional cotton	20	21
Bt cotton	3	4
Paddy	3	4
Pigeonpea	2	3
Chickpea	3	2
Tomato	7	9
Brinjal	12	15
Okra	13	20
Chilli	3	4
Cabbage	4	8
Cucumber	2	2
Onion	2	4
Kheera	2	3
Leafy vegetables	2	8
Mari gold	3	3

t (cal)=0.89, non-significant

The data clearly indicated that the farmers in Enkepally used more number of chemical sprays compared to the farmers in Kothapally for almost all the crops grown in that area.

Two sample t-test assuming unequal variances showed that there are no significant differences among the farmers between the two villages with respect to plant protection practices, plant protection advice, confidence in use of chemicals, awareness on effect of pest control measures on health, awareness on pesticide residues, knowledge on IPM and chemical usage on different crops.

4.1.4.8 Commonly used chemicals by farmers on various crops

A considerable variation was observed in the frequency of applications of chemicals on various crops in the two villages and generally the usage pattern by the farmers of various insecticides appeared similar. On traditional cotton, mostly the conventional chemicals such as monocrotophos, endosulfan, cypermethrin, quinalphos and a neonicotinoid (imidacloprid) were used. Bt cotton received more number of sprays containing neo-nicotinoids (imidacloprid followed by acetamiprid), followed by monocrotophos, endosulfan and cypermethrin. Though the number of chemical sprays on the food crops were less, the application of phorate granules, quinalphos, endosulfan, monocrotophos and chlorpyriphos in paddy crop were taken up by some farmers, whereas no insecticides were used for the maize crop. Pigeonpea and chickpea crops were sprayed with endosulfan and monocrotophos twice based on the appearance of the pests. Vegetables with demand round the year in the market were the second group of crops, which were grown intensively throughout the year in both villages, naturally received higher number of sprays. It was found that farmers not only used traditional

chemicals such as endosulfan, monocrotophos, cypermethrin and fenvalerate, but also used neo-nicotinoids such as imidacloprid, acetamiprid and other new molecules like spinosad, indoxacarb, interprid, and emamectin benzoate. However, popular molecules like monocrotophos, endosulfan, cypermethrin, and fenvalerate dominated the plant protection scenario among the insecticides used in both the villages.

4.1.5 Method Validation

4.1.5.1 Linearity

The gas chromatographic conditions yielded satisfactory separation of analytes. The individual insecticide standards of monocrotophos, chlorpyriphos, endosulfan I, endosulfan II and cypermethrin which were run in scan mode did not show any merging peaks. Later the same standards, which were run in selected ion monitoring (SIM) mode also showed good resolution. The standard insecticide mixtures at concentrations of 0.05, 0.1, 0.2, and 0.5 and 1.0 μg ml^{-1} were injected in GC-MS QP 5050 A. All the analyte peaks were clear without any merging. The GC-MS response for all analytes was linear in the concentration range (0.05-1.0 μg ml^{-1}) assayed with correlation coefficients >0.998. The correlation coefficient for monocrotophos, chlorpyriphos, endosulfan I, endosulfan II and cypermethrin I was R^2=0.999, and the correlation coefficient for cypermethrin II, cypermethrin III and cypermethrin IV was R^2=0.998. Blanks were run and no interference from the sample matrix was observed. Representative chromatograms of a standard insecticide mixture are shown in Fig. 1-3. The target analytes were searched at their stated retention times and were identified by comparing the mass spectra obtained with the known spectra of standard analytes. Retention times and standard areas of individual insecticide are given in table 40. The linearity graphs

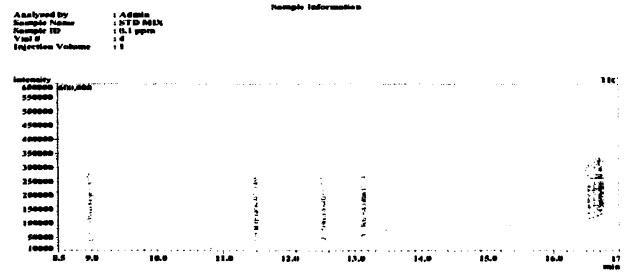


Fig 01: Chromatogram of 0.1 µg ml^{-1} standard insecticide mixture

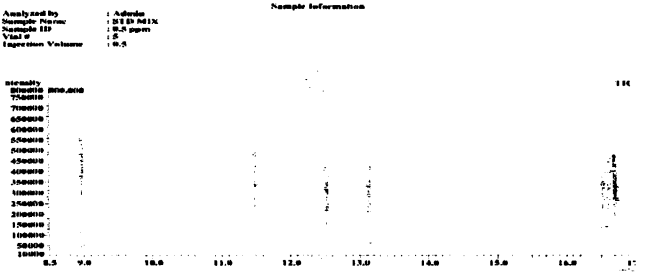


Fig 02: Chromatogram of 0.5 µg ml^{-1} standard insecticide mixture

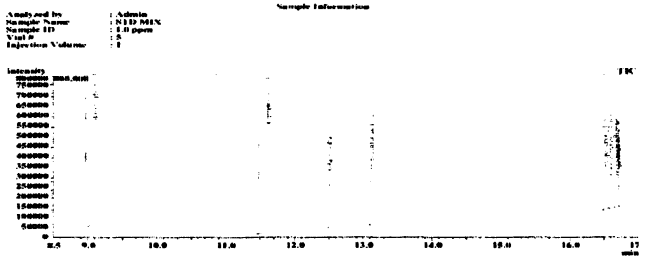


Fig 03: Chromatogram of 1.0 µg ml^{-1} standard insecticide mixture

Table 40: Retention times and standard areas of insecticide standards at different concentrations

Analyte	Concentration ($\mu g\ ml^{-1}$ or ppm)	Retention Time (RT)	Standard area / Intensity
	0.05	8.976	30127
	0.1	8.975	95852
Monocrotophos	0.2	8.976	151428
	0.5	8.971	393981
	1.0	8.97	870686
	0.05	11.488	28424
	0.1	11.488	54857
Chlorpyriphos	0.2	11.487	105537
	0.5	11.486	333346
	1.0	11.487	624820
	0.05	12.518	11638
	0.1	12.517	24650
Alpha Endosulfan	0.2	12.518	52628
	0.5	12.518	157534
	1.0	12.517	312783
	0.05	13.126	17812
	0.1	13.124	37065
Beta Endosulfan	0.2	13.125	70444
	0.5	13.128	202545
	1.0	13.122	401598
	0.05	16.529	16499
	0.1	16.534	31863
Cypermethrin I	0.2	16.531	61291
	0.5	16.531	184771
	1.0	16.529	371959
	0.05	16.616	15920
	0.1	16.616	30393
Cypermethrin II	0.2	16.616	58882
	0.5	16.615	168097
	1.0	16.613	354468
	0.05	16.7	16439
	0.1	16.697	26586
Cypermethrin III	0.2	16.698	57850
	0.5	16.698	146648
	1.0	16.696	320199
	0.05	16.727	21440
	0.1	16.713	20234
Cypermethrin IV	0.2	16.728	40587
	0.5	16.728	119795
	1.0	16.726	229171

for monocrotophos, chlorpyriphos, endosulfan I, endosulfan II, cypermethrin (four isomers) were shown in Graphs 6-13.

4.1.5.2 Recovery of insecticides

The reproducibility of the results for all the analytes was 76.6% and above for all the matrices. However, the mean average reading of a particular type of matrix analysed in triplicate was considered.

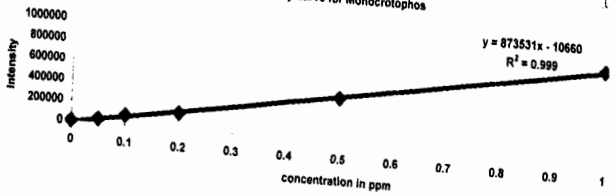
4.1.5.2.1 Recovery of insecticides in food crops and cotton lint samples

Tables 41-44 show the results on the recovery per cent of the insecticides in rice, maize, pigeonpea and cotton lint fortified with 0.025 and 0.01 μg g^{-1} insecticide mixture using liquid-liquid extraction. Recoveries obtained for all the analytes varied from 84.62 to 117.92% with relative standard deviation (RSD) between 2.11 and 8.23 for rice, 83.07 to 103.01% with RSD between 0.76 and 7.41 for maize, 79.09 to 101.8% with RSD between 2.10 and 5.88 for pigeonpea and 85.14 to 105.83% with RSD between 2.66 and 9.90 for cotton lint (Graphs 14 and 15). Chromatograms of control and fortified samples of food crops are shown in Fig. 4-15.

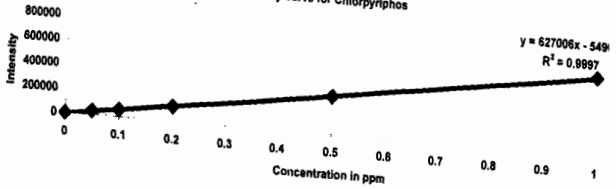
4.1.5.2.2 Recovery of insecticides in vegetables

The average percentage recovery of the insecticides in vegetables fortified at 0.025 and 0.005 μg g^{-1} levels was found to be more than 75% (Graphs 16 and 17). However, organochlorines showed higher recoveries than the organophosphates in the case of tomato. The recovery per cent in tomato ranged from 83.20 to 112.07% with relative standard deviation (RSD) between 0.39 and 8.48, whereas in brinjal the recovery was in the range of 76.66 to 105.80% with

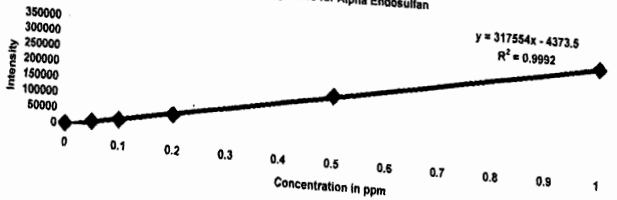
Graph 6 : Linearity curve for Monocrotophos



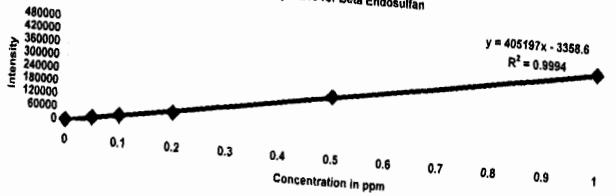
Graph 7 : Linearity curve for Chlorpyriphos



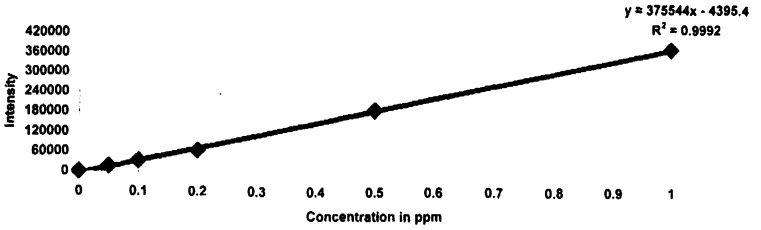
Graph 8 : Linearity curve for Alpha Endosulfan



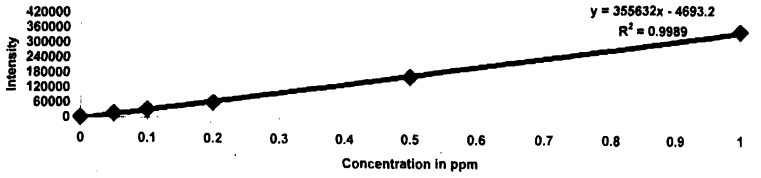
Graph 9 : Linearity curve for Beta Endosulfan



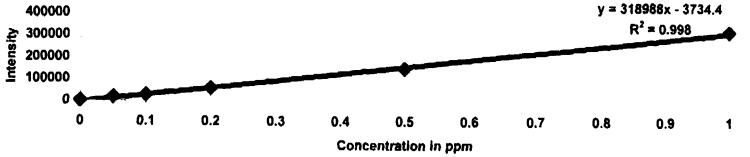
Graph 10 : Linearity curve for Cypermethrin-I



Graph 11 : Linearity curve for Cypermethrin-II



Graph 12 : Linearity curve for Cypermethrin-III



Graph 13 : Linearity curve for Cypermethrin-IV

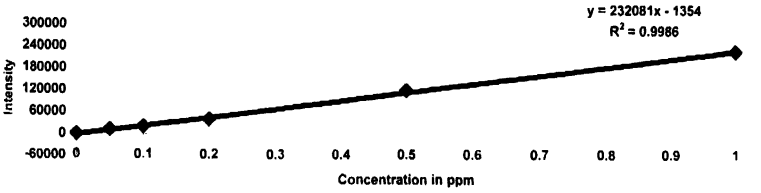


Table 41: Recovery per cent, mean and relative standard deviation in rice fortified at 0.01 μg g^{-1} and 0.025 μg g^{-1}

Fortification level (μg g^{-1})	Analyte	Recovery per centage				
		Replications			Mean ± SD	RSD %
		R_1	R_2	R_3		
0.01	Monocrotophos	101.34	105.67	103.01	103.34 ± 2.18	2.11
	Chlorpyriphos	95.77	103.28	99.78	99.61 ± 3.76	3.77
	Alpha Endosulfan	99.55	92.40	101.72	97.89 ± 4.87	4.98
	Beta Endosulfan	119.35	112.99	121.41	117.92 ± 4.39	3.72
	Cypermethrin (sum of four isomers)	104.38	120.15	104.71	109.75 ± 9.01	8.21
0.025	Monocrotophos	104.98	114.51	97.16	105.55 ± 8.69	8.23
	Chlorpyriphos	101.90	100.12	96.02	99.35 ± 3.01	3.03
	Alpha Endosulfan	87.60	82.22	84.04	84.62 ± 2.74	3.24
	Beta Endosulfan	118.69	118.95	109.41	115.68 ± 5.43	4.70
	Cypermethrin (sum of four isomers)	98.00	94.21	87.66	93.29 ± 5.23	5.61

Table 42: Recovery per cent, mean and relative standard deviation in maize fortified at 0.01 μg g^{-1} and 0.025 μg g^{-1}

Fortification level (μg g^{-1})	Analyte	Recovery per centage				
		Replications			Mean ± SD	RSD %
		R_1	R_2	R_3		
0.01	Monocrotophos	108.59	105.51	94.94	103.01±7.16	6.95
	Chlorpyriphos	90.67	91.98	90.94	91.20±0.69	0.76
	Alpha Endosulfan	96.98	92.01	91.39	93.46±3.07	3.28
	Beta Endosulfan	97.71	92.89	101.60	97.40±4.36	4.48
	Cypermethrin (sum of four isomers)	98.48	93.10	98.20	96.59±3.03	3.13
0.025	Monocrotophos	109.12	99.18	95.37	101.23 ± 7.10	7.01
	Chlorpyriphos	98.46	93.11	104.92	98.83 ± 5.91	5.98
	Alpha Endosulfan	106.28	91.64	98.57	98.83 ± 7.32	7.41
	Beta Endosulfan	89.87	100.25	98.09	96.07 ± 5.48	5.70
	Cypermethrin (sum of four isomers)	84.45	83.47	81.29	83.07 ± 1.62	1.95

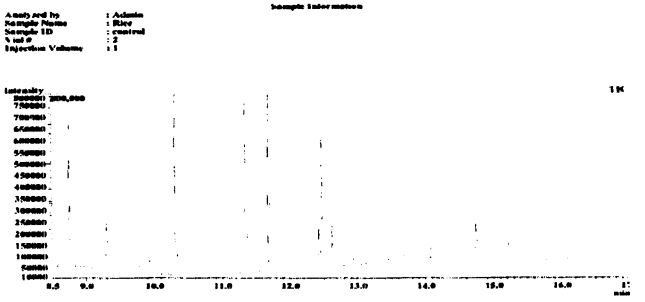


Fig 04: Chromatogram of rice grain control sample

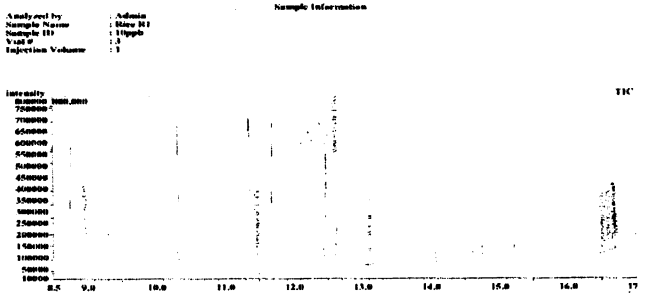


Fig 05: Chromatogram of rice grain sample fortified at 0.01 μg g^{-1}

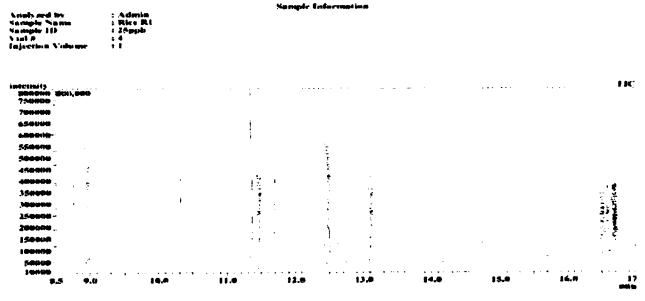


Fig 06: Chromatogram of rice grain sample fortified at 0.025 μg g^{-1}

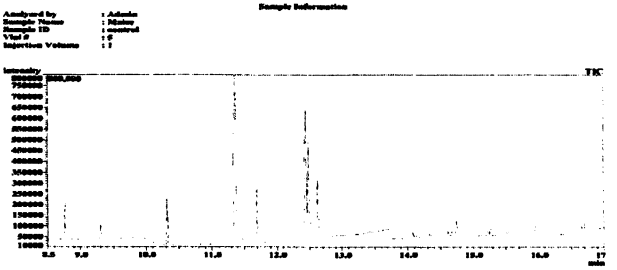


Fig 07: Chromatogram of maize grain control sample

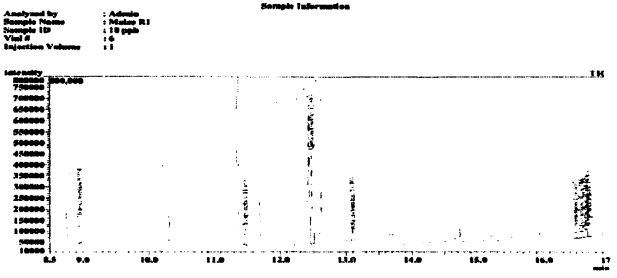


Fig 08: Chromatogram of maize grain sample fortified at 0.01 $\mu g\ g^{-1}$

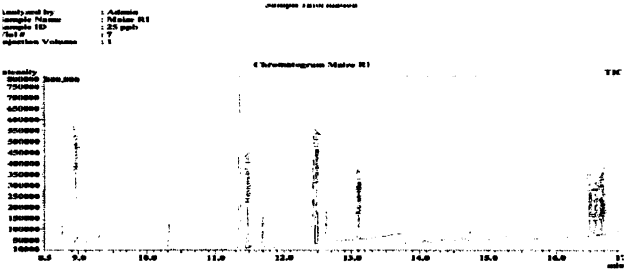


Fig 09: Chromatogram of maize grain sample fortified at 0.025 $\mu g\ g^{-1}$

Table 43: Recovery per cent, mean and relative standard deviation in pigeonpea fortified at 0.01 μg g^{-1} and 0.025 μg g^{-1}

Fortification level (μg g^{-1})	Analyte	Recovery per centage				
		Replications			Mean ± SD	RSD
		R_1	R_2	R_3		%
0.01	Monocrotophos	96.03	86.13	92.62	91.59 ± 5.03	5.49
	Chlorpyriphos	97.82	97.34	101.14	98.77 ± 2.07	2.10
	Alpha Endosulfan	93.80	91.57	88.49	91.28 ± 2.66	2.92
	Beta Endosulfan	100.28	93.60	89.27	94.38 ± 5.55	5.88
	Cypermethrin (sum of four isomers)	86.30	88.52	90.46	88.43 ± 2.08	2.35
0.025	Monocrotophos	104.86	98.18	102.44	101.83 ± 3.38	3.32
	Chlorpyriphos	98.85	92.93	98.69	96.82 ± 3.37	3.48
	Alpha Endosulfan	101.01	94.02	98.46	97.83 ± 3.54	3.61
	Beta Endosulfan	96.52	102.73	99.41	99.55 ± 3.11	3.12
	Cypermethrin (sum of four isomers)	79.04	81.10	77.13	79.09 ± 1.98	2.51

Table 44: Recovery per cent, mean and relative standard deviation in cotton lint fortified at 0.01 μg g^{-1} and 0.025 μg g^{-1}

Fortification level (μg g^{-1})	Analyte	Recovery per centage				
		Replications			Mean ± SD	RSD
		R_1	R_2	R_3		%
0.01	Monocrotophos	96.99	89.53	92.55	93.02 ± 3.75	4.03
	Chlorpyriphos	98.12	93.20	100.49	97.27 ± 3.72	3.82
	Alpha Endosulfan	97.72	100.50	83.20	93.81 ± 9.29	9.90
	Beta Endosulfan	106.09	93.27	94.93	98.10 ± 6.97	7.11
	Cypermethrin (sum of four isomers)	94.31	89.71	98.81	94.27 ± 4.55	4.83
0.025	Monocrotophos	93.54	98.75	103.39	98.56 ± 4.93	5.00
	Chlorpyriphos	110.05	105.99	101.46	105.83 ± 4.30	4.06
	Alpha Endosulfan	87.41	89.73	96.37	91.17 ± 4.65	5.10
	Beta Endosulfan	98.19	93.37	94.39	95.32 ± 2.54	2.66
	Cypermethrin (sum of four isomers)	88.47	84.95	81.99	85.14 ± 3.24	3.81

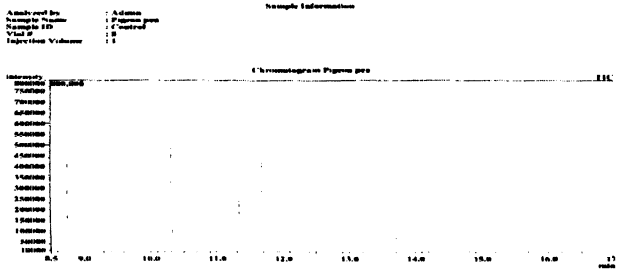


Fig 10: Chromatogram of pigeonpea grain control sample

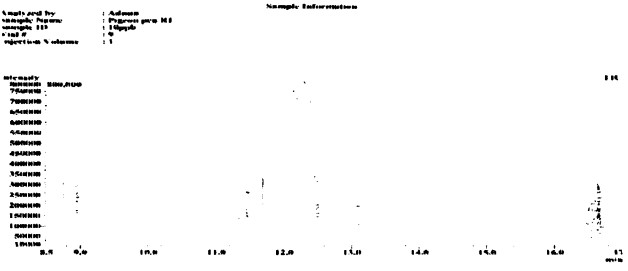


Fig 11: Chromatogram of pigeonpea grain sample fortified at 0.01 μg g^{-1}

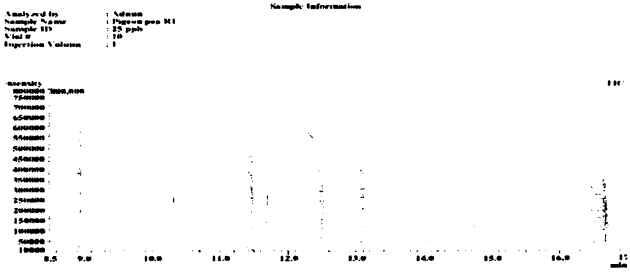


Fig 12: Chromatogram of pigeonpea grain sample fortified at 0.025 μg g^{-1}

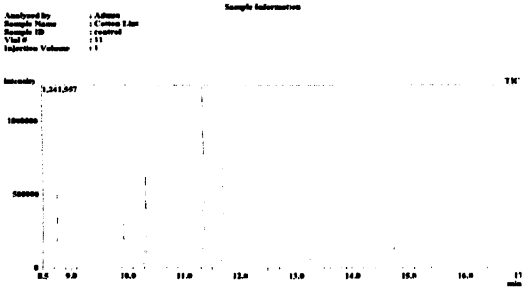


Fig 13: Chromatogram of cotton lint control sample

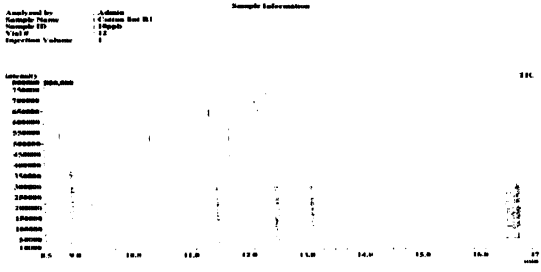


Fig 14: Chromatogram of cotton lint sample fortified at 0.01 $\mu g\ g^{-1}$

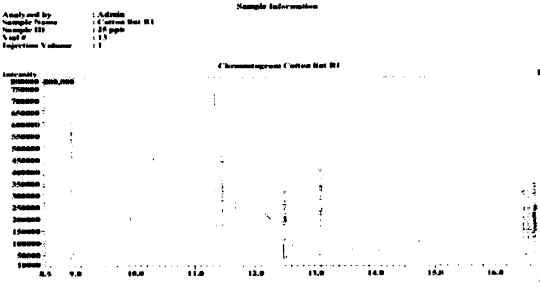
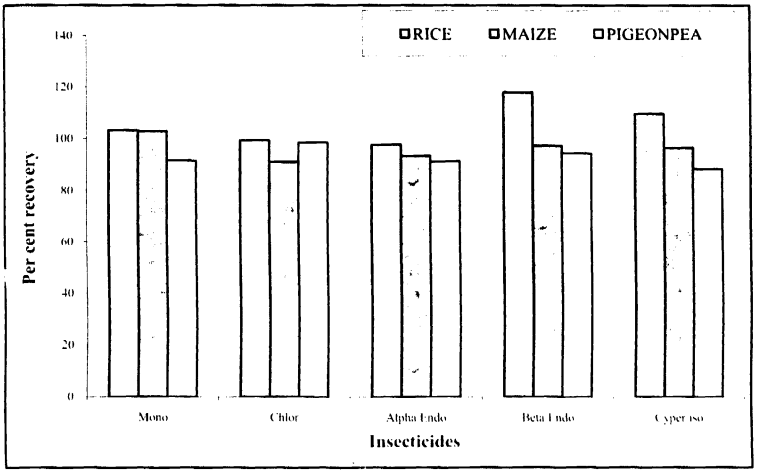
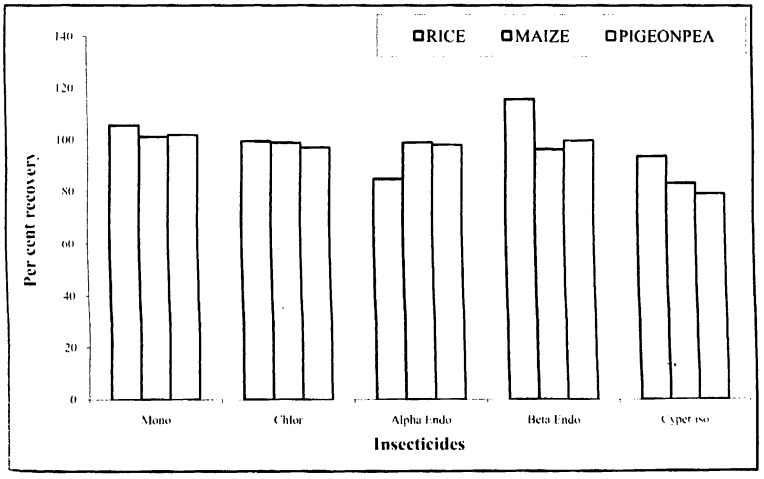


Fig 15: Chromatogram of cotton lint sample fortified at 0.025 $\mu g\ g^{-1}$



Graph 14: Per cent recovery of insecticides in food crops at 0.01 ppm fortification level



Graph 15: Per cent recovery of insecticides in food crops at 0.025 ppm fortification level

RSD between 1.90 and 7.82. The data are given in tables 45 and 46. Chromatograms of control and fortified vegetable samples are shown in Fig. 16-21.

4.1.5.2.3 Recovery of various insecticides added to the soil

The average recovery of insecticides from soil spiked at 0.025 and 0.001 μg g^{-1} following soxhlet method of extraction ranged from 80.23 to 104.08% with RSD between 4.17 to 11.85 (Table 47, Graph 18). Chromatograms of control and fortified soil samples are presented in Fig. 22-24.

4.1.5.2.4 Recovery of various insecticides added to water

The results on the recovery of insecticides applied to water samples are given in table 48 and Graph 19. The recovery of insecticides evaluated ranged from 82.81 to 109.39% with RSD between 1.50 and 6.86 after extraction with dichloromethane. Chromatograms of control and fortified water samples are presented in Fig. 25-27.

4.1.5.3 Limit of quantification and detection of the various insecticides used in the study

4.1.5.3.1 Limit of quantification and detection of various insecticides in food crops and cotton lint samples

An Acceptable recovery was obtained in the analysis of rice, maize, pigeonpea and cotton lint samples at the 0.01 μg g^{-1} spiking level and it was taken as the limit of quantification, and the limit of detection was found to be 0.003 μg g^{-1}.

4.1.5.3.2 Limit of quantification and detection in vegetables

From fortification experiment, it was evident that 0.005 μg g^{-1} was quantification limit for all the analytes in tomato and brinjal fruit samples with

Table 45: Recovery per cent, mean and relative standard deviation in tomato fortified at 0.005 μg g^{-1} and 0.025 μg g^{-1}

Fortification level (μg g^{-1})	Analyte	Recovery per centage				
		Replications			Mean ± SD	RSD %
		R_1	R_2	R_3		
0.005	Monocrotophos	85.90	98.17	85.86	89.98 ± 7.10	7.89
	Chlorpyriphos	101.18	90.58	98.47	96.74 ± 5.51	5.69
	Alpha Endosulfan	95.14	97.22	106.58	99.65 ± 6.09	6.11
	Beta Endosulfan	106.91	101.51	90.35	99.59 ± 8.45	8.48
	Cypermethrin (sum of four isomers)	86.55	82.64	94.39	87.86 ± 5.99	6.81
0.025	Monocrotophos	86.17	98.17	85.86	89.98 ± 7.10	7.89
	Chlorpyriphos	98.91	90.58	98.47	96.74 ± 5.51	5.69
	Alpha Endosulfan	115.86	97.22	106.58	99.65 ± 6.09	6.11
	Beta Endosulfan	96.85	101.51	90.35	99.59 ± 8.45	8.48
	Cypermethrin (sum of four isomers)	76.36	82.64	94.39	87.86 ± 5.99	6.81

Table 46: Recovery per cent, mean and relative standard deviation in brinjal fortified at 0.005 μg g^{-1} and 0.025 μg g^{-1}

Fortification level (μg g^{-1})	Analyte	Recovery per centage				
		Replications			Mean ± SD	RSD %
		R_1	R_2	R_3		
0.005	Monocrotophos	74.94	79.09	75.95	76.66 ± 2.17	2.82
	Chlorpyriphos	81.36	91.17	84.76	85.76 ± 4.98	5.81
	Alpha Endosulfan	99.55	91.12	85.25	91.97 ± 7.19	7.82
	Beta Endosulfan	89.65	92.64	98.21	93.50 ± 4.34	4.64
	Cypermethrin (sum of four isomers)	88.82	85.77	89.91	88.17 ± 2.15	2.44
0.025	Monocrotophos	93.14	96.96	93.18	94.43 ± 2.19	2.32
	Chlorpyriphos	104.02	105.05	108.32	105.80 ± 2.25	2.12
	Alpha Endosulfan	102.53	105.99	102.64	103.72 ± 1.97	1.90
	Beta Endosulfan	101.45	94.01	106.28	100.58 ± 6.18	6.15
	Cypermethrin (sum of four isomers)	94.13	104.74	98.93	99.27 ± 5.31	5.35

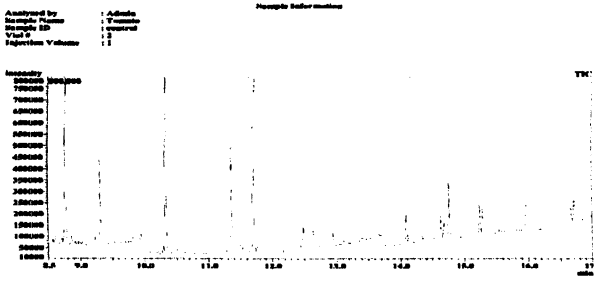


Fig 16: Chromatogram of tomato control sample

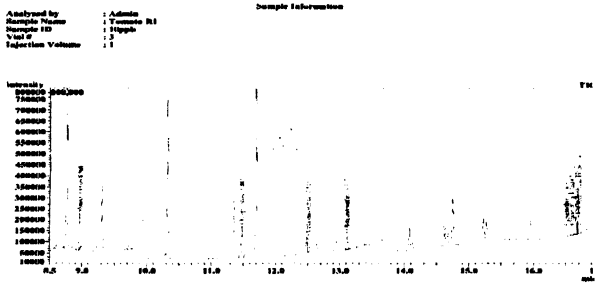


Fig 17: Chromatogram of tomato sample fortified at 0.005 µg g^{-1}

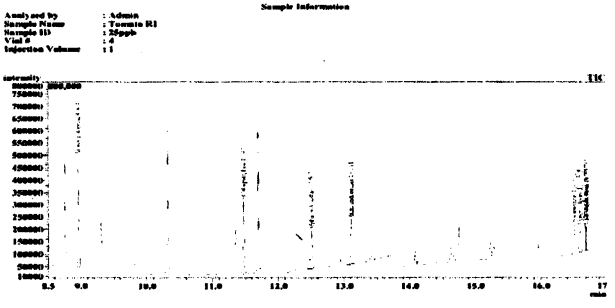


Fig 18: Chromatogram of tomato sample fortified at 0.025 µg g^{-1}

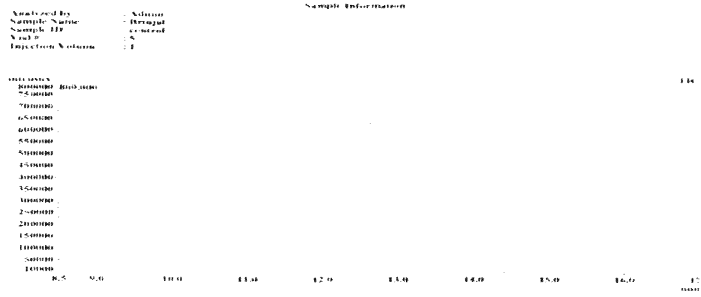


Fig 19: Chromatogram of brinjal control sample

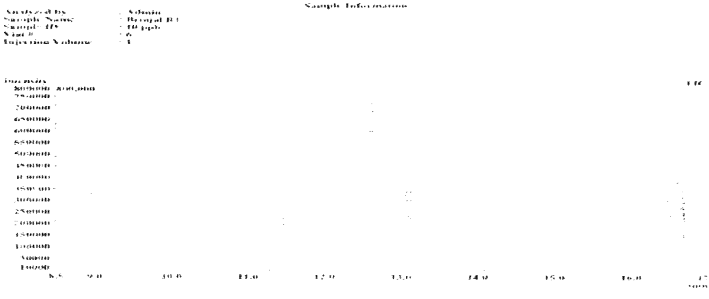


Fig 20: Chromatogram of brinjal sample fortified at 0.005 µg g^{-1}

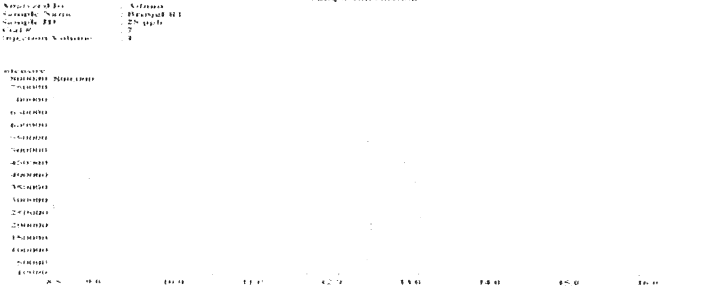
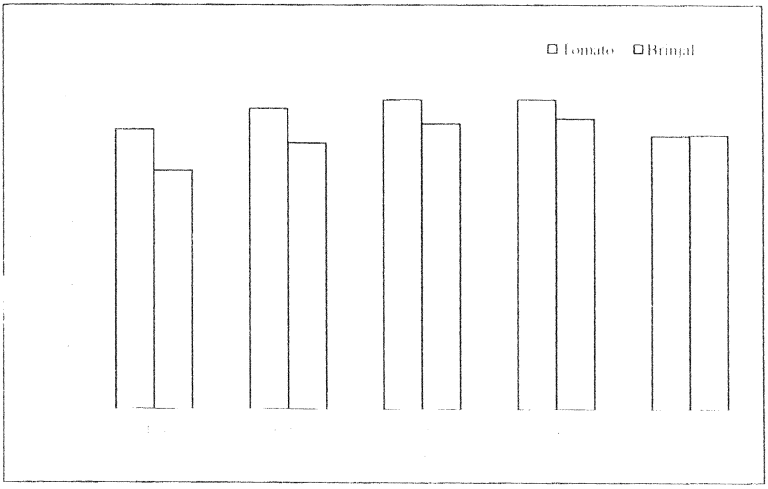
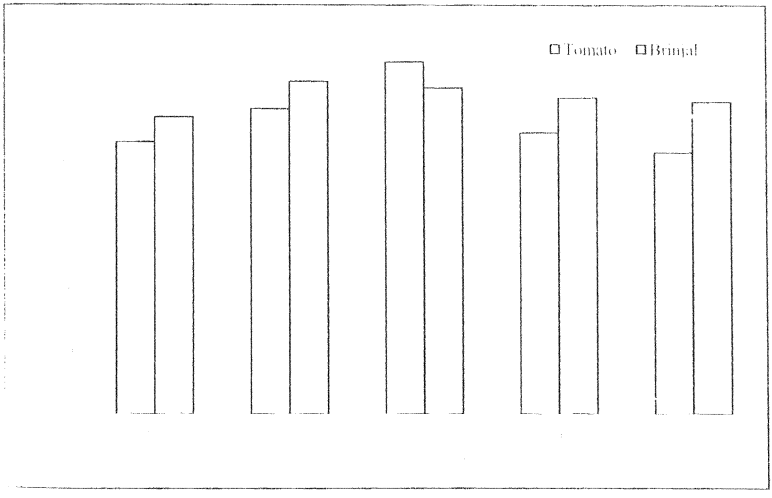


Fig 21: Chromatogram of brinjal sample fortified at 0.025 µg g^{-1}



Graph 16: Per cent recovery of insecticides in vegetables at 0.005 ppm fortification level



Graph 17: Per cent recovery of insecticides in vegetables at 0.025 ppm fortification level

Table 47: Recovery per cent, mean and relative standard deviation in soil fortified at 0.01 μg g^{-1} and 0.025 μg g^{-1}

Fortification level (μg g^{-1})	Analyte	Recovery per centage				
		Replications			Mean ± SD	RSD %
		R_1	R_2	R_3		
0.01	Monocrotophos	98.10	109.67	104.47	104.08 ± 5.79	5.57
	Chlorpyriphos	98.72	97.99	79.46	92.06 ± 10.91	11.85
	Alpha Endosulfan	76.75	73.40	90.77	80.31 ± 9.21	11.47
	Beta Endosulfan	75.72	80.11	84.86	80.23 ± 4.57	5.70
	Cypermethrin (sum of four isomers)	83.21	90.45	87.08	86.91 ± 3.62	4.17
0.001	Monocrotophos	92.98	101.33	84.74	93.02 ± 8.29	8.92
	Chlorpyriphos	97.06	85.38	96.82	93.09 ± 6.67	7.17
	Alpha Endosulfan	100.36	89.88	109.33	99.86 ± 9.73	9.75
	Beta Endosulfan	94.98	84.37	99.31	92.89 ± 7.69	8.28
	Cypermethrin (sum of four isomers)	93.48	87.16	96.89	92.51 ± 4.94	5.34

Table 48: Recovery per cent, mean and relative standard deviation in water fortified at 0.0005 μg ml^{-1} and 0.001 μg ml^{-1}

Fortification level (μg ml^{-1})	Analyte	Recovery per centage				
		Replications			Mean ± SD	RSD %
		R_1	R_2	R_3		
0.0005	Monocrotophos	90.54	94.99	96.69	94.07 ± 3.17	3.37
	Chlorpyriphos	95.36	104.90	98.52	99.60 ± 4.86	4.88
	Alpha Endosulfan	107.41	111.99	108.76	109.39 ± 2.36	2.15
	Beta Endosulfan	88.92	97.02	96.33	94.09 ± 4.49	4.77
	Cypermethrin (sum of four isomers)	97.99	95.18	97.22	96.80 ± 1.45	1.50
0.001	Monocrotophos	102.24	104.77	105.76	104.25 ± 1.81	1.74
	Chlorpyriphos	81.17	84.76	82.51	82.81 ± 1.81	2.19
	Alpha Endosulfan	98.36	89.56	95.95	94.62 ± 4.55	4.81
	Beta Endosulfan	91.82	95.59	89.71	92.37 ± 2.98	3.22
	Cypermethrin (sum of four isomers)	108.20	113.09	98.69	106.66 ±7.32	6.86

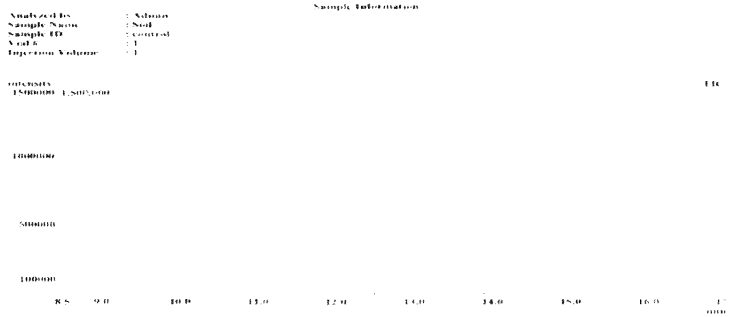


Fig 22: Chromatogram of soil control sample

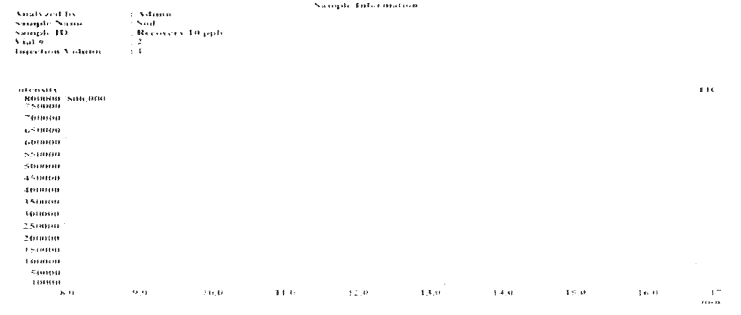


Fig 23: Chromatogram of soil sample fortified at 0.005 μg g^{-1}

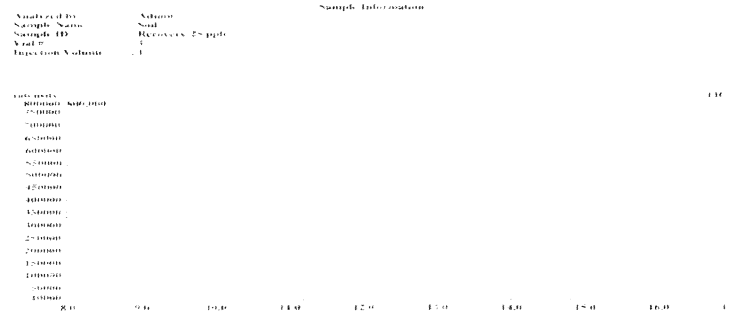


Fig 24: Chromatogram of soil sample fortified at 0.025 μg g^{-1}

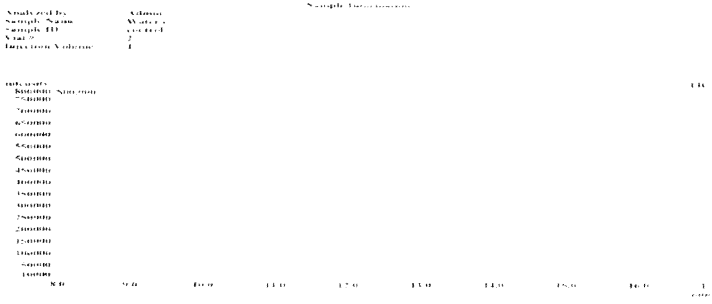


Fig 25: Chromatogram of water control sample

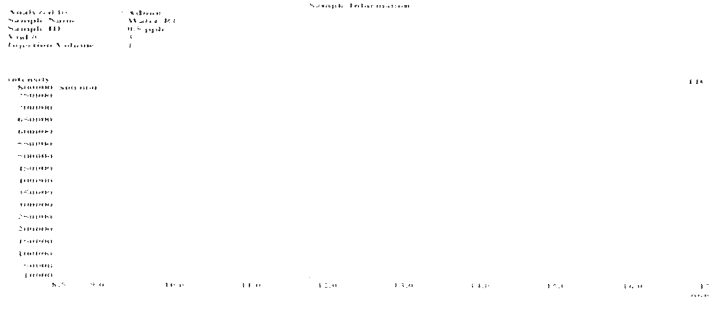


Fig 26: Chromatogram of water sample fortified at 0.005 µg ml $^{-1}$

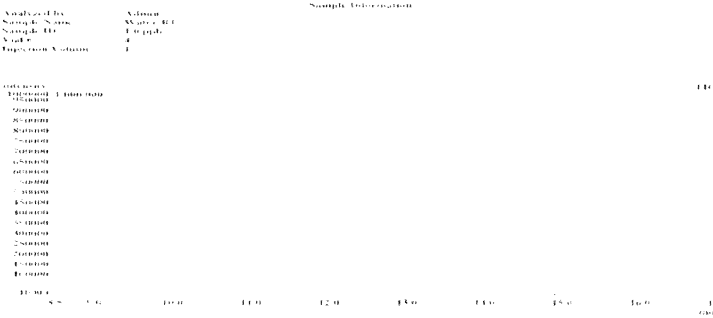
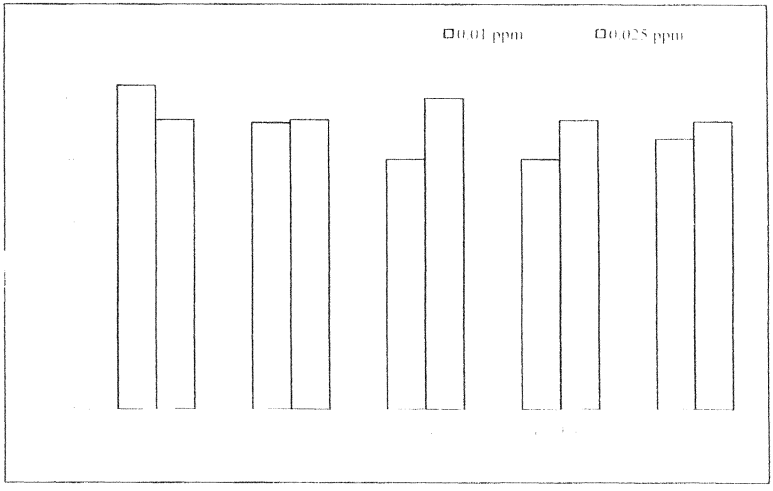
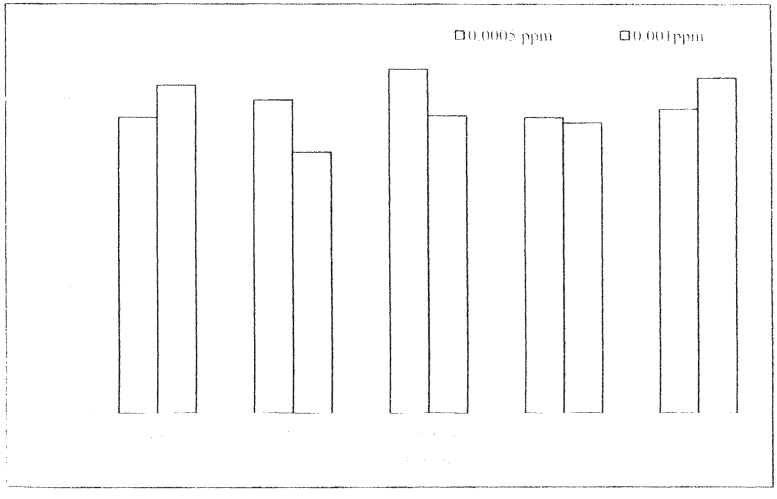


Fig 27: Chromatogram of water sample fortified at 0.025 µg ml $^{-1}$



Graph 18: Per cent recovery of insecticides in soil at 0.01 and 0.025 ppm fortification level



Graph 19: Per cent recovery of insecticides in water at 0.0005 and 0.001 ppm fortification level

acceptable range of RSD and limit of detection was three times less than limit of quantification which accounted to 0.001 $\mu g\ g^{-1}$.

4.1.5.3.3 Limit of Quantification and detection in the analysis of insecticide residues in the soil

An acceptable recovery of the insecticides, with RSD <12, was obtained when the soil samples were fortified with a concentration of 0.01 $\mu g\ g^{-1}$ and analysed following the extraction of the samples using soxhlet. This value (0.01 $\mu g\ g^{-1}$) was taken as the limit of quantification and therefore the limit of insecticide detection was 0.003 $\mu g\ g^{-1}$.

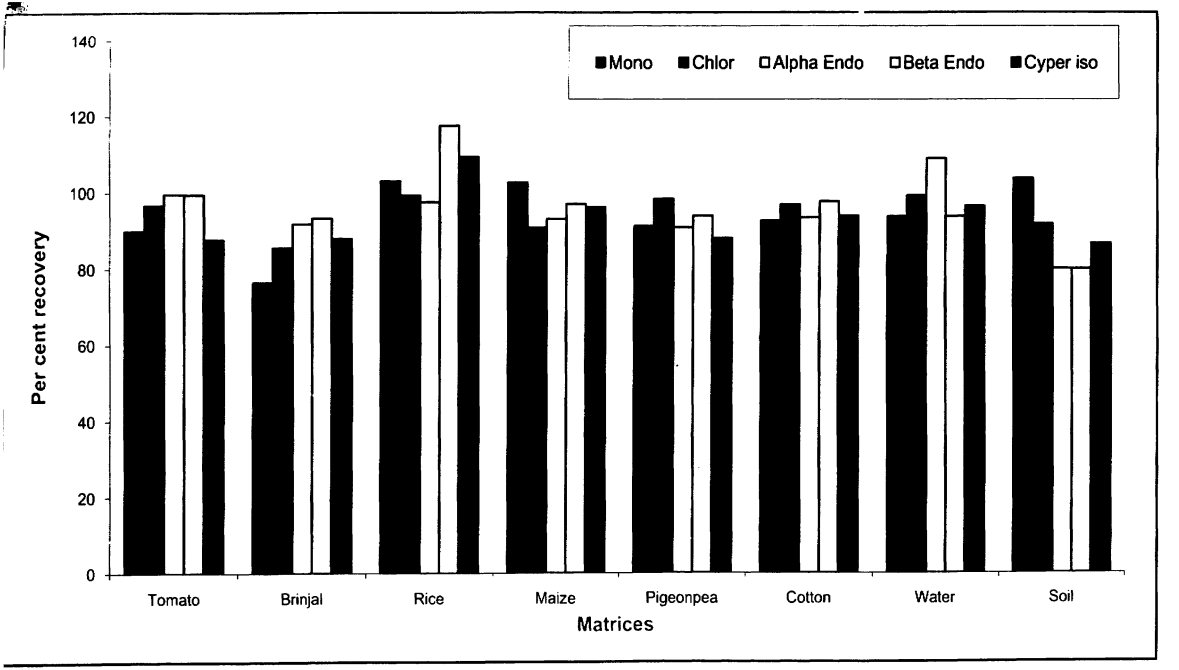
4.1.5.3.4 Limit of Quantification and detection in the analysis of insecticides added to water

Water samples fortified with insecticide concentration of 0.001 $\mu g\ ml^{-1}$ level gave an acceptable recovery with low RSD, which was considered as limit of quantification of the method. The limit of detection for water was 0.0003 $\mu g\ ml^{-1}$. The limit of quantification and detection for various matrices are given in table 49. Per cent recovery of insecticides in different matrices at LOQ and at five times the LOQ fortification level are presented in Graphs 20 and 21.

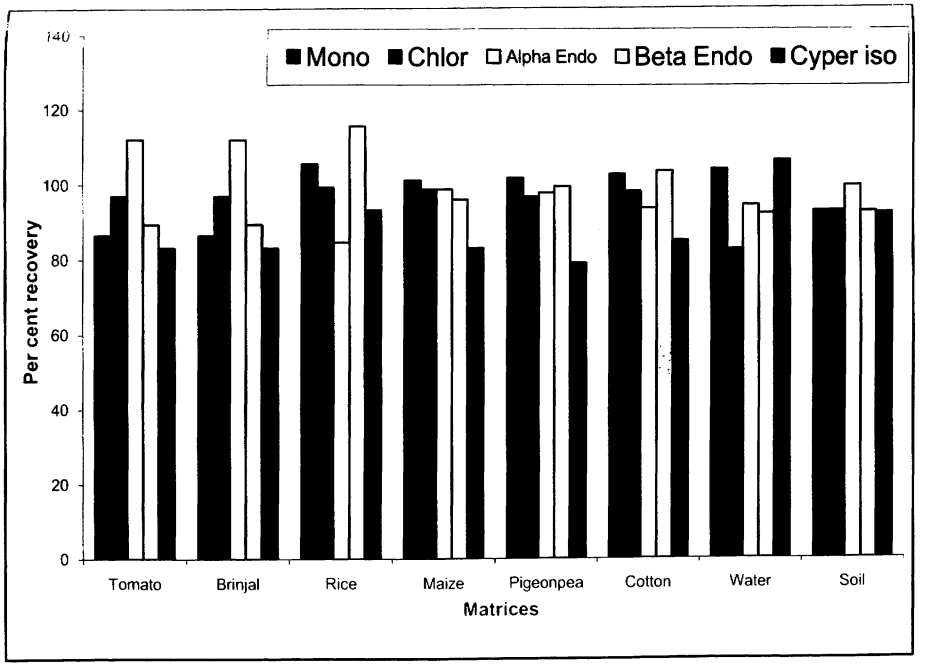
4.2 EVALUATION OF THE IMPACT OF IPM IN REDUCING INSECTICIDE RESIDUES

The samples of tomato and brinjal fruits, soil and water collected from non-IPM and IPM fields were analysed for insecticides *viz.*, monocrotophos, chlorpyriphos, alpha endosulfan, beta endosulfan and cypermethrin residues and the results are presented in tables 50, 51, 52 and 53.

Out of the 15 tomato fruit samples analysed for insecticide residues from IPM fields, only 3 samples (20% contamination) were found to contain



Graph 20: **Per cent recovery of insecticides in different matrices at LOQ fortification level**



Graph 21: **Per cent recovery of insecticides in different matrices at five times LOQ fortification level**

Table 49: Limit of quantification (LOQ) and Limit of detection (LOD) in different matrices

Matrix	LOQ ($\mu g\ g^{-1}$ or $\mu g\ ml^{-1}$)	LOD ($\mu g\ g^{-1}$ or $\mu g\ ml^{-1}$)
Tomato	0.005	0.001
Brinjal	0.005	0.001
Rice	0.01	0.003
Maize	0.01	0.003
Pigeonpea	0.01	0.003
Cotton lint	0.01	0.003
Soil	0.01	0.003
Water	0.001	0.0003

Table 50: Number of samples contaminated and range of insecticide residues (μg g^{-1}) in IPM and Non-IPM tomato crop, soil and water from Kothapally and Enkepally

Village	Season	Different sample matrices with insecticide residues in μg g^{-1}														
		Fruit[a]					Soil[b]					Water[c]				
		1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
Kothapally* IPM	Summer, 2009	ND	ND	ND	ND	3 (0.01-0.05)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

		Different sample matrices with insecticide residues in μg g^{-1}														
		Fruit[A]					Soil[B]					Water[C]				
		1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
Enkepally** Non-IPM	Summer, 2009	2 (0.05-0.09)	ND	1 (0.09)	2 (0.03-0.4)	5 (0.008-0.08)	ND	ND	1 (0.8)	ND	1 (0.04)	ND	ND	ND	ND	ND

*-No. of farmers (5), **- No. of farmers (5)
a-No. of fruit samples analysed (15), b-No. of soil samples analysed (10), c-No. of water samples analysed (10)
A-No. of fruit samples analysed (15), B-No. of soil samples analysed (10), C-No. of water samples analysed (10)
1-Monocrotophos, 2-Chlorpyriphos, 3-Alpha endosulfan, 4-Beta endosulfan, 5-Cypermethrin

Table 51: Number of samples contaminated and range of insecticide residues (μg g^{-1}) in IPM and Non-IPM brinjal crop, soil and water from Kothapally and Enkepally

Village	Season	Different sample matrices with insecticide residues in μg g^{-1}														
		Fruit[a]					Soil[b]					Water[c]				
		1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
Kothapally* IPM	Summer, 2009	ND	ND	ND	ND	3 (0.01-0.05)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

		Different sample matrices with insecticide residues in μg g^{-1}														
		Fruit[A]					Soil[B]					Water[C]				
		1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
Enkepally** Non-IPM	Summer, 2009	2 (0.05-0.09)	ND	1 (0.09)	2 (0.03-0.4)	5 (0.008-0.08)	ND	ND	1 (0.8)	ND	1 (0.04)	ND	ND	ND	ND	ND

*-No. of farmers (5), **- No. of farmers (5)
a-No. of fruit samples analysed (15), b-No. of soil samples analysed (10), c-No. of water samples analysed (10)
A-No. of fruit samples analysed (15), B-No. of soil samples analysed (10), C-No. of water samples analysed (10)
1-Monocrotophos, 2-Chlorpyriphos, 3-Alpha endosulfan, 4-Beta endosulfan, 5-Cypermethrin

Table 52: Insecticide Residues in IPM and Non-IPM tomato fruit, soil and water samples from Kothapally and Enkepally

Matrix	No. of samples		Insecticides detected	Frequencies	Residue level (μg g^{-1})	MRL (μg g^{-1})
	Analysed	Contaminated				
IPM						
Fruit	15	3	Cypermethrin	3	0.05, 0.02, 0.01	0.5
Soil	10	0	...	...	...	...
Water	10	0	...	...	...	...
Non-IPM						
Fruit	15	7	Monocrotophos	2	0.09, 0.05	0.2
			Alpha endosulfan	1	0.09	2.0
			Beta endosulfan	2	0.4, 0.03	2.0
			Cypermethrin	5	0.05, 0.08, 0.008, 0.009, 0.01,	0.5
Soil	10	2	Alpha endosulfan	1	0.8	2.0
			Cypermethrin	1	0.04	2.0
Water	10	...	...	...	...	...

Table 53: Insecticide Residues in IPM and Non-IPM brinjal fruit, soil and water samples from Kothapally and Enkepally

Matrix	No. of samples		Insecticides detected	Frequencies	Residue level ($\mu g\ g^{-1}$)	MRL ($\mu g\ g^{-1}$)
	Analysed	Contaminated				
IPM						
Fruit	15	3	Monocrotophos	1	0.005	0.2
			Beta endosulfan	1	0.1	2.0
			Cypermethrin	1	0.1	0.5
Soil	10	0	...	...	...	...
Water	10	0	...	...	...	...
Non-IPM						
Fruit	15	7	Monocrotophos	3	0.01, 0.03, 0.09	0.2
			Alpha endosulfan	3	0.07, 0.009, 0.01	2.0
			Beta endosulfan	2	0.006, 0.08	2.0
			Cypermethrin	3	0.02, 0.01, 0.04	0.5
Soil	10	2	Chlorpyriphos	1	0.03	Not available
			Alpha endosulfan	1	0.01	Not available
Water	10	0	...	...	...	...

cypermethrin residues in the range of 0.01-0.05 μg g^{-1}. None of the soil and water samples collected from IPM fields contained insecticide residues. Fourty seven per cent of the tomato fruit samples from non-IPM fields were contaminated with different insecticide residues with a concentration ranging from 0.008 to 0.4 μg g^{-1}. Two soil samples out of the 10 samples analysed, were found to contain residues of alpha endosulfan (0.8 μg g^{-1}) and cypermethrin (0.04 μg g^{-1}). However, no water sample contained the residues above the detectable level. The residue levels of insecticides detected from IPM and non-IPM samples were found to be below the MRL.

Monocrotophos, beta endosulfan and cypermethrin residues were detected in 20% of the brinjal samples under IPM treatment and the residue concentration ranged from 0.005 to 0.1 μg g^{-1}. Soil and water samples collected from IPM fields did not contain insecticide residue.

Out of the 15 brinjal samples under the non-IPM treatment analysed, 7 samples (47% contamination) contained the residues of all insecticides except for chlorpyriphos. The incidence level of monocrotophos, alpha endosulfan and cypermethrin was 3 in each case and beta endosulfan was identified twice. The residue concentration ranged from 0.006 to 0.09 μg g^{-1}. Chlorpyriphos and alpha endosulfan residues were detected in two soil samples and 20% of the samples were contaminated, and residue concentration ranged from 0.01 to 0.03 μg g^{-1}. As in the case of tomato, the residues of none of the insecticides were detected at or above the prescribed MRLs in brinjal and related matrices from the IPM as well as in non-IPM treatments.

DISCUSSION

CHAPTER V

DISCUSSION

Although farmers are using insecticides more frequently, even higher than the recommended dose, the damage reduction is not up to the expected extent. This might be due to the circumstantial increase in the selection pressure of insecticide on the insect causing resistance among the target population. The farmers' decision to spray is influenced more by the visual presence of the pest rather than guided by the economic thresholds. Considering the high expenditure involved in the use insecticide, any tactic, which will reduce the use of insecticides, will make crop cultivation more remunerative and with reduced chance of the insecticide residue in the produce. Therefore, it is important to monitor the insecticide residue to determine whether the farmers are complying with the recommended doses of insecticides. Integrated pest management (IPM) strategy offers the opportunity to reduce the insecticide residues on crops. The salient results of present investigation on **"Status of Insecticide Residues and Impact of Integrated Pest Management"** are discussed below.

5.1 MONITORING INSECTICIDE RESIDUES IN VARIOUS CROPS AND MATRICES

5.1.1 Monitoring Insecticide Residues in Food Crops, Cotton, Soil and Water from Kothapally (IPM) and Enkepally (Non-IPM) Villages during 2008 and 2009

Analysis of samples from food crops, tomato and brinjal collected from farmers' fields indicated the presence of residues of various groups of insecticides.

The differences in the residue concentrations could have been due to differences in crop, location, insecticide used, timing of sampling the crop and the agro-climatic conditions during the season and at the time of sampling. According to Chattopadhyay (1998), the persistence of insecticide depends on the prevailing temperature and time lapsed between spraying and harvesting of the crop. The insecticide residues also varied from contact to the non-contact village in the same matrix, which could be due to differences in the method and rate of insecticide application. The results might also be influenced by the method used for the preparation and analysis especially the method used for the extraction of insecticide residues. The presence of an insecticide residue in a sample or multiple insecticide residues in a sample might be due to the application of more than one insecticide on a crop during the growing season and possible drift of persistent residues in the environment.

Measurement of insecticide residues in rice grains, soil and water at harvest showed the presence of only endosulfan residues in grain and soil which could be attributed to the fact that farmers used endosulfan for pest control in the Paddy fields as indicated during the survey (see section 4.1.3.8). Our results are also supported by the findings of Kannathasan and Regupathy (1992) and Ahuja and Awasthi (1993) who reported that rice grain contained organochlorine insecticide (HCH and DDT) residues and the concentrations were 0.001 mg kg^{-1} and 0.0049-0.0505 mg kg^{-1} for α and β-HCH, respectively.

The present finding on the presence of endosulfan residues in rice soils are supported by reports of Battu *et al.* (1989) who found that the soils from rice

plots treated at 2.5 and 5 kg a.i. ha^{-1} of HCH at the time of flowering showed residue concentrations of 0.023 and 0.157 $\mu g\ g^{-1}$ at the harvest time.

Although none of the farmers accepted the application of chemicals on the maize crop according to the survey, the analysis of maize grain, soil and water samples indicated the presence of endosulfan residues only in the soil. This might be due to the application of endosulfan granules in the maize whorls for the control of borers or due to the prolonged persistence of endosulfan isomers in the environment or could be due to drift from adjoining fields which received insecticide sprays frequently. The absence of endosulfan residues in maize grains may be due to the dissipation of endosulfan or the respective farmer might not have used any chemical on the crop and this finding is in consonance with the study conducted by Singh *et al.* (1992) who reported that the residues of endosulfan in maize cobs were below the detectable level after 11-20 days following application at 0.05, 0.1 and 0.2% at 60 days and 90 days after sowing. However, Kavadia *et al.* (1979) found the residue to the extent of 1.5 mg kg^{-1} at harvest (after about 48 days of last spraying) after three sprayings of endosulfan (0.1%).

Pigeonpea grain at harvest did not show any insecticide residues in our study though monocrotophos and endosulfan were used two times by the farmers depending on the pest incidence on the crop. Our findings can be partially justified by the reports of Dethe *et al.* (1991) who indicated that the measurement of endosulfan residues in pigeonpea grains at harvest showed no detectable levels of the residue when applied twice at 15 days interval starting at 50% flowering. The following findings of different workers partly agree with the present study.

Senapati *et al.* (1992) found that the residues of endosulfan, monocrotophos and quinalphos were more concentrated in the husk than in the grain and suggested that neither grain nor husk be consumed following application of quinalphos and monocrotophos but that the grains may be safely consumed after treatment with endosulfan. Study by Singh and Hameed (1991) showed the safety intervals of 28 days for monocrotophos residues following its application at the rates of 0.5 and 1.0 kg a.i. ha^{-1} at 50% flowering and 50% pod formation stage in pigeonpea grains and straw. The harvested samples of blackgram and greengram contained non-detectable level of chlorpyriphos when applied at the rate of 0.5 and 1.0 kg a.i. ha^{-1} one month after sowing and at pod initiation stage (Samant *et al.*, 1997). The residues of endosulfan sprayed at the vegetative, flowering and pod formation stages of the black gram crop were below the detectable level in the harvested grain, whereas when sprayed at the maturity, the residue concentration varied from 0.05 to 0.09 $\mu g\ g^{-1}$ and it was evident that endosulfan should not be sprayed at the maturity stage of the crop (Nayak *et al.*, 2004).

The non detection of residues in soils from pigeonpea fields are in agreement with the results of Tanwar and Handa (1998) who found that the residues of endosulfan in the soil from the spray of endosulfan on the pigeonpea crop were below the detectable limit at harvest of the crop.

The cotton lint samples were found with no detectable residues. The reason could be attributed to shift in cotton cultivation from traditional to Bt varieties, which requires less number of sprays according to survey. Kumar (1998), Suganthy (2003), Suganya Kanna *et al.* (2007) also found the residues of imidacloprid and acetamiprid in cotton lint at below detectable levels.

These results are in agreement with the findings of Gupta *et al.* (1998) who reported no residues in cotton lint from the treatment of seeds with imidacloprid. However, some results from the literature are partly in disagreement with our results.

For example, four sprays each of cypermethrin (50 g a.i. ha^{-1}), deltamethrin (15 g a.i. ha^{-1}), fenvelarate (75 g a.i. ha^{-1}) and endosulfan (700 g a.i. ha^{-1}) at 10 day interval on a 90 day cotton crop resulted in cypermethrin residues at non-detectable levels but endosulfan at 0.84 mg kg^{-1} in cotton seed at the time of first picking (Yadav *et al.*, 1993) and cotton lint contained beta cyfluthrin residues at 0.3 and 0.4 mg kg^{-1} following application at 12.50 and 18.75 g a.i. ha^{-1} at 50% flowering which could be due to binding of the chemical with cellulose present in the lint and availability of more surface area (Battu *et al.*, 1999).

5.1.2 Monitoring Insecticide Residues in Vegetables (Tomato and Brinjal), Soil and Water Samples Collected from Kothapally and Enkepally during Various Seasons in 2008 and 2009

The monitoring of insecticide residues in brinjal and tomato samples during 2008-2009 revealed that out of 85 (45 tomato and 40 brinjal) and 70 (30 tomato and 40 brinjal) vegetable samples analyzed from Kothapally and Enkepally, 34 and 61% of samples were contaminated, respectively.

A consistent trend in the level of contamination in tomato fruit samples from the Enkepally was observed during the summer (67%) and *kharif* (50%) seasons in 2008 and 2009. However, a decreasing trend in the insecticide residues was observed in samples from the Kothapally during the same period.

A decreasing trend in the contamination level in the brinjal samples was noticed during summer (58% to 50%) and *kharif* (63% to 58%) seasons 2008 to 2009 in Kothapally, while the results from the Enkepally indicated an increasing trend (75% to 88%) during the summer and a decreasing trend (75% to 63%) during the *kharif* season.

The results can be compared with those reported by Kiran Kumar Reddy (2008) who found that the incidence as well as level of insecticidal contamination of seasonal vegetable and water samples with monocrotophos, chlorpyriphos, endosulfan and cypermethrin decreased significantly in selected villages in the Ranga Reddy district, which can be probably attributed to change in the usage pattern of insecticides. The insecticides are being replaced with new chemistries like neonicotinoids (imidacloprid, acetamiprid, thiamethaxam), spinosad, indoxacarb and avermectins (emamectin benzoate and abamectin), which are easily degradable and do not persist for longer periods in the environment.

The present study showed the presence of monocrotophos in selected vegetable samples above MRL concentrations due to unauthorized sale by pesticide dealers and use by farmers, although this insecticide is banned for use on vegetables as per the Insecticide Act, 1968 as on 28th December, 2006 (Sharma, 2007).

5.1.3 Monitoring Insecticide Residues in Soils

A decreasing trend was observed in samples from Kothapally -- from 33% to 17% and 50% to 0% in the 2008 and 2009 summer and *kharif* seasons, respectively. An increase in contamination percentage was observed from 25% to 50% in Enkepally during summer, 2008 and 2009.

The fate of insecticides in the environment depends on biotic and abiotic factors including the presence and population of microorganism that degrade the insecticide, agro-climatic conditions such as temperature and rainfall, soil properties such as pH, moisture, texture and organic matter content of soil. These factors vary from site to site depending on season and the chemistry of the soil, resulting in different rates of degradation and residue concentration of the insecticides at different sites (Lal, 1983 and Van Veen *et al.*, 1997). Rao and Hornsby (2001) reported that soil type affected the persistence degradation and retention of organochlorine pesticide residues.

Pyrethroids though sufficiently stable in environment (Elliot, 1980), suffered rapid decomposition in tropical soils compared to their temperate counterparts mainly through hydrolysis at the ester linkage in the molecule (Chapman and Harris, 1981). The sandy loam soil experienced rapid decomposition (Awasthi, 1997), while accelerated decomposition of pesticides was reported in mineral as compared to organic soils (Roberts, 1981).

The contamination of soil samples with insecticide residues from the field planted with brinjal was lower as compared to the samples from the field planted with tomato. This could be attributed to greater canopy cover under brinjal and longer duration of the crop. Jayashree and Vasudevan (2007) indicated that high cover by the paddy canopy could lose greater concentrations of pesticide in soil and pesticide load in the run-off.

The occurrence of higher concentrations of residues in fruit and soil samples from the non-contact village could be due to indiscriminate use, untimely application, low quality formulations and the lack of appropriate crop rotation.

However, the survey clearly indicated that the number of insecticide sprays on a particular crop was greater in Enkepally than in Kothapally.

5.1.4 Monitoring Insecticide Residues in Water Samples

None of the samples collected from the sources that supply water to vegetable fields collected during different seasons showed any insecticide residues. This could be attributed to the hydrophobicity of the organochlorines and pyrethroids. According to the WHO (2004), most of the organochlorine pesticides are practically insoluble in water. Our results are in agreement with the findings of Jagdishwar Reddy *et al.* (1997) who reported that monitoring of organochlorines, organophosphates and pyrethroids in river, tank and canal water showed no residues of organophosphates and pyrethroids, but the organochlorines such as DDT, BHC were detected. However, most of the documented review on pesticide residues in water in India indicated the presence of highly persistent organochlorines like DDT, HCH, lindane, and heptachlor and endosulfan in different water sources. Since the pyrethroids are strongly hydrophobic in character, their residues did not stay in water and therefore travelled across the water depth down to settle on fine sediment. The suspended residues were severely dealt with by the percolating Sunrays and decomposed rapidly through photo degradation reaction and hence pyrethroids did not persist longer in the surface or bottom water layers (Awasthi, 1997). The rapid loss of permethrin (Rawn *et al.*, 1982) and deltamethrin (Muir *et al.*, 1985) in pond water with a half life of less than one day was observed due to their rapid partitioning into suspended solids and finally sinking at the bottom of the pond along with the sediments.

Other reasons for non detection of residues in water could be the timing and the frequency of sampling, low levels of residues in crop and soil samples, less sensitivity of liquid- liquid extraction method, the insecticides monitored in the study would have declined gradually. The crops would not have received considerable number of insecticide sprays to the level to leave the residues at the beginning and end of the crop season. Domagalski (1997) showed that the sampling of surface water three times in a week in the San Joaquin River Basin had two-times greater probability to detect the pesticide residue concentrations exceeding the state water standards than did a single weekly sampling. Carter (2000) found that three 200 μm diameter spray droplets from a spray mix containing 1 kg ha^{-1} active substance can cause contamination of one liter of water to 0.12 μg l^{-1}. The results indicated that the residue levels were lower in the crop and soil samples because by the time they reach water bodies, the residues would have been dissipated. Moreover, the insecticides chosen for monitoring in our study are applied to canopy directly and there would be lower probability of the residues reaching the soil and water bodies.

As majority of the samples in the present study were found to contain residues at non-detectable levels or at concentrations less than MRLs of the respective insecticides, the present pattern of insecticide use in vegetable fields in both Kothapally and Enkepally does not seem to contribute towards excessive insecticide residues.

5.1.5 Farmers' Perception of Plant Protection in Kothapally and Enkepally

5.1.5.1 Initiation of plant protection and sources of plant protection advice

Majority of the farmers (80-86%) were not aware of the economic importance of various pests in their crops as they applied chemicals immediately after observing the pest or as a prophylactic. Thirty eight per cent of the farmers in Kothapally and 50% in Enkepally got their plant protection advice from pesticide dealers. Thirty five per cent and 20% of the farmers implemented plant protection according to the advice from the agricultural officers in Kothapally and Enkepally, respectively. It is evident from this study that farmer's knowledge on pest and their impact on yield was limited and the adoption of economic thresholds is rather complicated for them without technical back up from the research and the farmer-extension team work.

5.1.5.2 Farmer's confidence in the use of chemicals

Fourty per cent of farmers from Kothapally and 32% from Enkepally indicated that the poor efficacy was due to the presence of spurious pesticides in the market; and 14% (Kothapally) and 8% (Enkepally) of the farmers in these two villages felt that the poor efficacy was due to the development of resistance in pests to the chemicals used.

The farmer's confidence in chemicals to control pests is perhaps due to their immediate action; and they were not aware of harmful residual effects of excessive use and indiscriminate use of chemicals. Survey in Bangladesh indicated a strong farmer preference in favor of pesticides to control rice pests (Hossain *et al.*, 2000). Study conducted by Sharma *et al.* (2005) to find out the awareness level

of the farmers regarding the implications caused due to excessive use of pesticides, indicated that 28% of the respondents were not aware of the instructions written on the pesticide containers and more than 50% did not follow these instructions. Further, 65% of the respondents were not aware of the recommended dose, although they were aware of the environmental pollution being created due to the excessive use of pesticides. Encouraging farmer participatory research and up scaling extension would play a key role in improving the farmers' knowledge and confidence in the ongoing plant protection activities to address the present problems in the use of pest control chemicals including insecticide resistance, pest resurgence and pesticide residues (Mathews, 2001).

5.1.5.3 Awareness about health

Only 32% of the farmers in Kothapally and 12% in the Enkepally used protective clothing while applying the toxic plant protection chemicals. Amongst the various health problems, farmers complained headache as the major health problem followed by skin rash and eye irritation.

McConnen (2002) indicated that no farm worker in Ethiopia ignored the use of personal protective equipment while handling toxic chemicals. A study in Bangladesh by Hossain *et al.* (2000) indicated 98% of those that apply pesticides felt dizzy afterwards. There are several reports emphasizing the ill effects of pesticides associated with acute health problems for workers who handle the chemicals, such as abdominal pain, dizziness, headache, nausea, vomiting as well as skin and eye problems and long term health problems (McCauley *et al.*, 2006; Beseler *et al.*, 2008; Montgomery *et al.*, 2008). Though persistence of some pesticides was known to majority of the farmers (67%), only 36% respondents

were aware of the hazardous effects of their excessive use and 54% of farmers were unaware of ill effects (like asthma) and other respiratory and skin diseases and allergies caused by pesticides in human beings (Sharma *et al.*, 2005).

5.1.5.4 Knowledge about Integrated Pest Management (IPM)

Although 48% of farmers in Kothapally and 16% in Enkepally were aware of IPM, only half of them adopted it in Kothapally. The low adoption of IPM in various crops was primarily due to the non-availability of IPM inputs at farm level, the complexity of IPM modules for different crops, lack of information on the ill effects of toxic chemicals and the existing insufficient extension networks. A survey conducted by Blake *et al.* (2007) in the Massachusetts Cranberry grower community to identify the barriers to adoption of available IPM indicated that a large proportion of respondents agreed that IPM can reduce pesticide residues in food (92%) and the environment (96%), and can help to preserve beneficial insects (96%). Although many growers held the perception that IPM can pose measurable economic risk (and subsequently act as a barrier to adoption), growers appeared to feel less strongly about the economic benefits than potential environmental ones. Study by Mangat *et al.* (1998) to evaluate the adoption of IPM technology by cotton growers in Punjab indicated that only 18.67% of the farmers showed high adoption status, 50.67% showed medium adoption status and 30.66% showed low adoption status as many of the components of the technology did not favour cotton growers.

5.1.6 Validation of GC-MS (SIM) Method

5.1.6.1 Linearity

The standard insecticide mixtures at concentrations of 0.05, 0.1, 0.2, and 0.5 μg ml^{-1} injected in GC-MS QP 5050 A gave clear peaks without any merging.

The GC-MS response for all analytes was linear in the concentration range (0.05 - 0.5μg ml^{-1}) assayed with correlation coefficients > 0.998. The present findings are in agreement with the results by XueDong *et al.* (2008) who reported that linearity was obtained in the range of 0.05 to 40 μg kg^{-1} for malathion, 0.04 to 10 μg kg^{-1} for lambda-cyhalothrin and 0.05 to 50 μg kg^{-1} for cypermethrin, and the coefficients of correlation ranged from 0.9993 to 0.9998 using GC-ECD.

5.1.6.2 Recovery experiments with GC-MS

Recovery experiments exhibited efficacy of the extraction procedures for monocrotophos, chlorpyriphos, alpha endosulfan, beta endosulfan and cypermethrin in all the matrices studied (tomato, brinjal, rice, maize, pigeonpea, cotton lint, soil and water) at different spiking levels. Satisfactory recoveries were obtained with low (<10%) relative standard deviation (RSD). Average recoveries of the above insecticides at different fortification levels ranged from 76.6 to 117.92%. The variation in the recovery of different insecticides in different matrices might have been due to various factors including a probable degradation of insecticides during complete evaporation of the solvents by the rotary evaporator. The insecticides might have also been oxidized due to solvent evaporation through direct air (Lantos *et al.*, 1983). The poor recoveries of some of the insecticides might have been due to their high polarity and strong adsorption with florisil in the cartridge used for elution. A higher recovery of some of the insecticides used might have been due to matrix induced enhancement effect.

Recovery of insecticides from vegetables ranged from 83.2 to 112.07% at fortification levels of 0.005 and 0.025 μg g^{-1}. Our results are in agreement with the findings of Kole *et al.* (2002) and Rissato *et al.* (2005) who reported a recovery

range of 82 to 96% and 76 to 84% in brinjal and tomato at fortification levels of 0.5 and 1.0 mg kg^{-1} (Endosulfan, chlorpyriphos, monocrotophos and cypermethrin); and 0.05 (Alpha endosulfan and cypermethrin) and 0.06 mg kg^{-1} (Chlorpyriphos and beta endosulfan) by extracting with acetone, n-hexane; and solid-liquid extraction methods, respectively.

Spiking of insecticides in rice at 0.01 and 0.025 µg g^{-1} showed a recovery range of 84.62 to 117.92%. Cho *et al.* (2006) reported similar results who found a recovery range between 82.7 and 126.4% at spiking levels of 0.1 and 0.5 mg kg^{-1} of diazinon, EPN (O-ethyl-o-p-nitro phenyl phenylphosphonothionate) and isoprothiolane in polished rice following accelerated solvent extraction. The mean recovery of 95.73% was obtained by Nalini *et al.* (2003) from fortified rice grain at 0.5 µg g^{-1} spiking with betacyfluthrin by extracting with acetonitrile, n-hexane and dichloromethane. The various substrates of rice crop i.e. straw, bran, husk and grains fortified with 0.02 and 0.05 µg g^{-1} of different HCH isomers gave the average recoveries of greater than 80% (Battu *et al.*, 1989).

Pigeonpea matrix showed a recovery of 79.09 to 101.83% at 0.01 and 0.025 µg g^{-1} fortification levels. The average recovery of monocrotophos, fenvelarate, endosulfan was 83.88, 95 and 82.8, 98%, respectively, at different levels of spiking of pigeonpea (Singh and Hameed, 1991; Patel *et al.*, 1990; Tanwar and Handa, 1998).

Cotton lint spiked at 0.01 and 0.025 µg g^{-1} levels gave recovery of 85.14 to 105.83%. Our findings are in agreement with the results established by Singh *et al.* (2001) who found that average recovery of cypermethrin and ethion at different

levels of spiking in cotton lint following soxhlet extraction with acetone and hexane was greater than 80%.

An average recovery of 82.81 to 109.39% was recorded from HPLC grade water fortified at 0.0005 and 0.001 μg ml^{-1} levels. The recoveries from spiked sample of water with cypermethrin were 310.34 and 138.62% at spiking levels of 0.146 and 1.46 μg l^{-1} by liquid-liquid extraction with dichloromethane added at a concentration of 8.7 μg l^{-1} (Tahir *et al.*, 1999). Gupta *et al.* (2006) reported similar results who reported that a multiple-residue method developed for the estimation of organochlorine (dieldrin, p, p'-DDE, α-endosulfan, β-endosulfan, endosulfan sulphate, α, δ-HCH, γ-HCH) and organophosphorus (chlorpyriphos, alachlor, ethion, malathion, methyl parathion and phorate) groups of insecticides in water using GLC-ECD with dichloromethane as the extraction solvent, gave recoveries > 80% at 0.1 and 1.0 μg l^{-1} fortification levels with LODs between 0.001 to 0.01 μg ml^{-1} and LOQs between 0.1 to 1.0 μg l^{-1}.

The mean recovery range of 80.23 to 104.08% (RSD from 4.17 to 11.85) was obtained from the soil sample spiked at 0.01 and 0.025 μg g^{-1} concentrations following the soxhlet method of extraction. These results are in agreement with those, which reported that cypermethrin added at 8.7 μg kg^{-1} fortification level gave a recovery of 147.05% using the soxhlet extraction method (Tahir *et al.*, 1999) and chlorpyriphos added at 5.5 μg g^{-1} gave 95% recovery with chloroform as the extractant (Arora and Singh, 2004). Findings of Rissato *et al.* (2005) which showed recoveries ranging from 70 to 97% for majority of the pesticides added to the soil at 0.04 to 0.10 mg kg^{-1} also support the results obtained in the present study.

The overall RSD for each matrix and the RSD at each fortification level was <20%. The mean recovery at each fortification level for the matrices used was

in the range of 70-110%, which are in accordance with the figures reported in the Guidance Document on Pesticide Residue Analytical Methods (OECD, 2007).

5.2 EVALUATION OF THE IMPACT OF IPM IN REDUCING INSECTICIDE RESIDUES

Out of the 15 tomato fruit samples analysed for insecticide residues from IPM fields, only 3 samples (20% contamination) were contaminated while non-IPM fields showed 47 % contamination. None of the soil and water samples collected from IPM fields contained insecticide residues. Two soil samples from non-IPM fields contained residues. The residue levels of insecticides detected from IPM and non-IPM samples were found to be below the MRL.

Out of the 15 brinjal samples under the non-IPM treatment analysed, 7 samples (47% contamination) contained the residues.

The results on the impact of IPM in reducing insecticide residues clearly indicated a demarcation in insecticide residues between IPM and non-IPM vegetable fields. The recorded contamination per cent of residues from non-IPM fields was almost double than that of IPM fields. It was evident from the survey results that more number of insecticide sprays was applied in the Enkepally compared to that in the Kothapally, which could be the probable reason for the presence of insecticide residues in greater number of samples from the Enkepally. These results are in agreement with the findings of Sardana *et al.* (2004, 2005) who found that the use of neem seed kernel extract (NSKE) intermittently with insecticides and other biological and mechanical practices as a part of IPM package, resulted in increased yield and the harvested brinjal from non-IPM package had higher amount (above MRL) of the residues of monocrotophos (1.25 mg kg^{-1}); and the residues of chlorpyriphos, monocrotophos and

cypermethrin were 1.54, 6.72, 3.76 μg g^{-1} in non-IPM fields of okra and were higher than those recorded for the IPM fields.

Similar findings were reported by Arora and Singh (2004) who reported that the residues of chlorpyriphos and cypermethrin in okra were found to be 0.1 μg g^{-1} and non detectable from IPM trails and 5.75 and 0.63 μg g^{-1} from the non-IPM fields while that of monocrotophos in brinjal fruits were found to be non detectable and 1.25 μg g^{-1} for IPM and non-IPM fields, respectively. Singh *et al.* (2008) found pesticide residues *viz.*, methyl parathion, chlorpyriphos, endosulfan, cypermethrin, fenvelerate, carbendazim, imidacloprid and carbaryl at below prescribed MRL in non-IPM samples, while the samples from the fields under IPM had no pesticide residues. Leandri *et al.* (1996) suggested that IPM strategies generally brought about an improvement in the quality of the tomato fruit with lower insecticide residue levels than in the fields under traditional schedules based on treatments at fixed intervals and this supports the findings in the present study.

As in the case of fruit samples, insecticide residues were detected in a few soil samples of non-IPM fields. This could be supported by the results reported by Arora and Singh (2004) on the residues of chlorpyriphos, cypermethrin and monocrotophos on okra and brinjal under IPM and non IPM treatments. The residue of chlorpyriphos in the soil at sowing was 0.41 μg g^{-1} and concentrations were 4.22 and 1.14 mg g^{-1} at harvest in samples from non-IPM and IPM okra fields, respectively.

However, the use of insecticides should be need based only and recommended insecticides be applied as and when required depending on the economic thresholds. Further, to safeguard the interest of consumers, proper waiting period must be observed by the producer before marketing the vegetables.

SUMMARY

CHAPTER VI

SUMMARY

The present research was taken up to study the **"Status of insecticide residues and impact of Integrated Pest Management".** The field studies were conducted to monitor the insecticide residues on food crops (rice, maize, pigeonpea), cotton, vegetables, and in soil and water and to know the impact of Integrated Pest Management (IPM) in reducing insecticide residues in samples collected from farmers' fields. The laboratory experiments were conducted in Pesticide Residue Laboratory at the International Crops Research Institute for the Semi-Arid Tropics (ICRISAT), Patancheru, India. Participatory rural appraisal (PRA) was undertaken in Kothapally watershed (contact village) and Enkepally (non-contact village).

Residue analysis in the food crops and cotton for presence of insecticide residues (monocrotophos, chlorpyriphos, alpha endosulfan, beta endosulfan and cypermethrin) showed that one rice grain sample (0.5 $\mu g\ g^{-1}$) out of 5 samples collected from Kothapally was contaminated and among the soil samples, residues were detected in one (0.02 $\mu g\ g^{-1}$) out of 5 soil samples collected from maize field during 2008 in Enkepally. Only two samples were contaminated -- one rice grain sample (0.008 $\mu g\ g^{-1}$) and one soil sample (0.03 $\mu g\ g^{-1}$) collected from rice field during 2009 from Enkepally.

Monitoring of insecticide residues in vegetables indicated that out of the total 45 tomato fruit samples from Kothapally analysed over a period of five seasons in 2008 and 2009, 11 samples (24%) were found to contain residues. In Enkepally village, the residues were observed in 50% of samples (15 out of 30

samples) during this period. However, none of the samples from Kothapally and 7% of contaminated samples from Enkepally had residues above MRLs.

During 2008 and 2009, out of the 30 soil samples collected from tomato fields only six samples (20%) contained insecticide residues. Out of the 20 soil samples drawn from Enkepally, 7 (35%) were contaminated.

In Kothapally and Enkepally, 17 (43%) samples and 29 (73%) samples out of 40 samples contained insecticide residues, respectively. The overall residue levels in brinjal during the study period indicated 7% of samples in Enkepally above MRLs.

Soil sample analysis in five various seasons during 2008 and 2009 showed that only 10% and 15% of the samples collected from brinjal fields were contaminated in Kothapally and Enkepally, respectively. None of the water samples collected from food crops, cotton and vegetable crops were contaminated.

Thirty eight per cent of the farmers in Kothapally and 50% in Enkepally got their plant protection advice from pesticide dealers and on the other hand, 35% in Kothapally and 20% of the farmers in Enkepally adopted plant protection advice from the agricultural officers. Majority of farmers from Kothapally (40%) and Enkepally (32%) indicated that the poor efficacy of pesticides was due to the spurious pesticides in the market.

Only 32% of the farmers in Kothapally and 12% in the Enkepally used protective clothing while applying the toxic plant protection chemicals. Amongst the various health problems, farmers complained headache as the major health problem followed by skin rash and eye irritation.

Forty four per cent of the farmers in Kothapally and only 16% in Enkepally were aware of the residual effects of pesticides. Though the farmers were aware of a waiting period in reducing residues, only 30% of them were following the concept for a period of 2-5 days.

Although 48% of farmers in Kothapally and 16% in Enkepally were aware of IPM, only half of the farmers in Kothapally them adopted it. Traditionally cotton was found to be heavily sprayed crop with 20-21 sprays, followed by vegetables (2-20). Among the vegetables, okra received more insecticide sprays (13, 20), followed by brinjal (12, 15), tomato (7, 9), cabbage (4, 8) and leafy vegetables (2, 8). Among the insecticides used, popular molecules like monocrotophos, endosulfan, cypermethrin, and fenvelerate dominated the plant protection scenario in both the villages.

Out of the 15 tomato fruit samples analysed for insecticide residues from IPM fields, only 3 samples (20% contamination) were found to contain residues compared to 47% in Non-IPM fields. Two soil samples out of the 10 samples from non-IPM tomato fields analysed were found to contain residues.

In brinjal, 20% of the samples under IPM treatment and 47% in non-IPM had contamination. Twenty per cent of soils in non-IPM fields had residues while none of the soil samples in IPM fields had residues. Water sample collected either from IPM (or) non-IPM vegetable fields contained no residues above the detectable level. Though the contamination levels in crops and soils in IPM and non-IPM fields indicated substantial differences, the residue concentrations were below MRLs.

The GC-MS response for all analytes was linear in the concentration range of 0.05-1.0 $\mu g\ ml^{-1}$ assayed with correlation coefficients of >0.998.

The reproducibility of the results for all the analytes ranged from 76.6% to 117.92% with low (<10%) relative standard deviation for all the matrices which are acceptable levels.

Conclusions

- Analysis of samples from food crops, tomato and brinjal collected from farmers' fields indicated the presence of residues of various groups of insecticides.
- The contamination levels in food crops was low and below MRLs.
- Few vegetable samples showed contamination at or above MRLs and some had monocrotophos (banned insecticide) residue even at MRLs.
- Some soils showed insecticide residues indicating accumulation of residues in soil.
- All water samples were free from insecticide residues under study.
- IPM samples contained less residues compared to non-IPM samples.

Future line of work

- Monitoring of new molecule insecticide residueds may be taken up.
- Periodicity of sampling may be increased in case of soil and water.
- Implementation of IPM should be taken up on a large scale.
- More sensitive methods of extraction can be followed.

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APPENDIX

Questionnaire to generate information insecticide application in farmers' fields in Kothapally and neighbouring villages of RangaReddy district, Andhra Pradesh, 2008.

Village: Mandal: Date:

Name of the farmer:

1. Farming experience 2. Land holding

3. What are the common crops grown and the pest management practices adopted?

Year	Rainy season			Post rainy		
2006	Crop	Pest	No. of sprays/chemicals	Crop	Pest	No. of sprays/chemicals
2007						

4. How do you decide to apply chemicals? Calendar basis/ At appearance of pests/ By counting insects/ By following neighbour

5. From where do you get pest control advice? Neighbour/Block supervisor/Relatives/Pesticide dealers/Radio/TV

6. Are you aware of the failure of chemical pesticides since a few years? If yes, what do you think may be the reasons for the failure of pest control by pesticide? Unknown reasons/Low power of pesticides/ Duplicate pesticides/Resistance of pest to pesticides

7. Do you observe any health problems soon after pesticide spray? If yes, do you observe any of the following problems: Skin rash/Nausea/Headache/Eye irritation/Dizziness/Other problems:

8. Do you adopt protective measures during pesticide spray? If yes, which one? Cover face with cloth/Cover body and face with cloth/Wear a nose mask/Other measures

9. Are you aware of chemical/ pesticide residues?

10. Are you aware of precautions or safety period to avoid pesticide residues?

11. Are you aware of integrated pest management? If so what?
Cultural practices (Intercrops/Trap crops/Bird perches/Shaking)/Resistant varieties/Pheromones/Biopesticides (Neem/HNPV)/Trichogramma

Maximum Residue Limits in ppm as per Prevention of Food Adulteration Act, 1954 (updated 2007)

Chemical	Tomato	Brinjal	Milled Rice	Milled Maize	Milled Pigeonpea	Cotton lint	Soil	Water
Monocrotophos	0.2	0.2	0.006	0.006	0.006	Not available	Not available	0.1 ppb
Chlorpyriphos	0.2	0.2	0.01	0.01	0.01	Not available	Not available	0.1 ppb
Endosulfan (Alpha + Beta + Endosulfan sulphate)	2.0	2.0	Not available	Not available	0.1	Not available	Not available	0.1 ppb
Cypermethrin	0.5	0.2	Not available	Not available	Not available	Not available	Not available	0.1 ppb
For all pesticides								0.5 ppb