

Pesticide Residue in Selected Market Samples of Cereals and Pulses and Impact of Cooking

BY

M. Revathi



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Introduction

I INTRODUCTION

The present growth rate of world's population of about two per cent^{per} year adds nearly 2,00,000 people to the world each day. Demographers have projected that the world population will reach 6,000 - 7,000 million by the turn of the century and by the 22nd century, it will be 10,000 - 16,000 million (U.S. National Academy of Science, 1975). Food and Agricultural Organisation estimates that as many as 1,500 million individuals suffer from hunger and malnutrition. Most of these live in the developing countries largely in tropical or sub tropical zones (Gunn and Stevens, 1976). To meet the food requirement of such a population we will need to improve the world's current food output. To achieve such a goal, control of pests is indispensable.

Crop yields are considerably reduced by insects and pests. Crops are under constant attack by a wide range of insects and insects pests during all stages of their growth, transportation and storage. It is reported that the aggregate pre and post-harvest losses of food grains in India are of the order of about 50 per cent of total production. (Majumder et al., 1976). It has been estimated that of the total produce, 5.20 millions are lost through agricultural losses. Of this 5 to 10 per cent of the loss can still be prevented by intensifying the use of pesticides, in developed countries and 30 to

40 per cent could be saved by the judicious use of pesticides. In India, the losses due to various pests is estimated to be around Rs.6,000 crores per annum. Of this loss maximum damage is done by weeds (33 per cent) followed by plant diseases (26 per cent) and insect pests (20 per cent) while the storage loss could be at 7 per cent. Rats are estimated to cause about 6 per cent loss to standing crops (Banerjee, 1980).

India with a gross population of 68,38,10,051 covering an area of 32,87,782 sq km produced 10,88,50,000 tonnes of food grains during 1979-80 (India, 1981). Only 0.64 million hectares were under the plant production umbrella. According to Ministry of Agriculture, the plant production area during 1982-83 is expected to be 100 million hectares. There has been rapid progress in the production and consumption of pesticides over the past two decades. The demand for the use of pesticides increased from 11 to 25 per cent in the course of 20 years.

Although the over all pesticide growth rate may be impressive the rate of consumption per hectare of cultivated land is very low. Pesticide production and usage in India is quite low as compared to developing countries like Mexico where 750 g are used per hectare and Argentina 960 g per hectare. In developed countries

like U.S.A. and West Germany 3,000 g are used per hectare and in Japan, 11,800 g per hectare which is 10 times and 40 times respectively of the quantities and used in India (Sharma, 1981). This would be one of the major factors that could be attributed to low per hectare yields of food crops in India, since the crops especially the high yielding varieties cannot exhibit their production potential in the absence of proper pest production.

In India,⁴ due to climate factors, incidence of agriculture and stored product, pests is chronic and severe. Hygienic measures alone cannot fully control the insect infestation in agricultural crops and stored produce and the use of pesticide becomes necessary complement to the production and conservation of foods.

Therefore, pesticides have become an indispensable and permanent tool for modern strategy of crop production, agriculture where high yielding about short duration of crops are grown. Pesticides being basically toxic to man, their unrestricted use both in the field and ware houses lead to inevitable contamination of food materials, with these unintentional additives. So, the contamination will lead to consumer health hazards. The magnitude of pollution in India with special emphasis on

foodstuffs has been studied. The pesticides pollution problems due to pesticide usage in food and environment vary from region to region. Surveillance and monitoring programmes are also directly related to the pattern of usage of pesticide and socio-economic conditions of the region.

In India, the monitoring and surveillance of pesticide residues in various cereals and pulses are still inadequate. Studies on the nature and extent of contamination of food stuffs have been limited in scope and restricted to selected areas and to few compounds. The persistence of insecticide which are the pesticides mainly used on foods is of concern from the public health point of view.

Residue studies in cereals and pulses are important because they form the staple food of South India. Moreover, pesticides are used indiscriminately and some monitoring of pesticides residue on grains is essential.

This study therefore, involves the assessment of pesticides residues in selected cereals such as rice, ragi, sorghum and wheat and pulses like greengram dhal, bengal gram dhal, red gram dhal and black gram dhal collected from the local markets in Coimbatore. The residual effects after cooking was also studied.

Review of Literature

II REVIEW OF LITERATURE

Review of the literature pertaining to this study on Pesticide residue in selected market samples of cereals and pulses and impact of cooking is discussed under the following heads:

- A. Agricultural production and loss
- B. History on Pesticide usage and Pesticides in Vogue
- C. Classification of Pesticides
- D. Residual action of Pesticides
- E. Pesticide Residue in Water
- F. Pesticide Residue in Foods.

A. Agricultural Production and Loss:

It is estimated that on world wide basis about 20,000,000 tons of organic chemicals enter the environment annually. The solvents such as methanol, ethanol, alcohol, ether and chlorinated solvents account for about half of the chemicals entering the environment, detergents amount to 1.5 m.tons and organic pesticides to about 1 million ton (Niel, 1972). A report of the U.S. Department of Agriculture has indicated that a complete stop in the use of pesticides might result in a 25 to 30 per cent in crop and livestock production. United Nations Food and Agriculture Organisation plans to reduce food losses due to pests by

20-30 per cent as part of a drive to achieve four-fold increase in food supplied (Bloom, 1969). Crop yields are considerably reduced by insect pests. The losses are as high as 25 to 30 per cent of the total produce which exceed Rs.5,000/- crores annually. According to the National Council of Economic Research the maximum loss of 40.3 per cent was recorded in cotton 8.8 to 12.1 per cent was in paddy, jowar, sugarcane and potato and 2.8 per cent in wheat between 1950-1966. The plan evaluation of Planning Commission has estimated crop losses due to insect pests during 1967 as 17.807, 6.57, 11.91 and 12.90 per cent in paddy, maize, bajra and jowar respectively. From the above data, it is apparent that a large proportion of the farm produce is whisked away by insect pests. To avoid these losses, the use of insecticides to keep the pest population below economic level becomes very important (Sharma, 1981).

There has been rapid progress in the production and use of insecticide over the past two decades in India. The initial production of 432 tonnes in year 1954 had risen to 40,658 tonnes by 1977. Considering the trend of consumption, it had increased from 434 tonnes in 1954 to 58,980 tonnes by 1977-'78. Projections for increase in pesticide consumption during the early half of this decade is at the rate of 6 per cent per annum. (Prasad, 1976 and David, 1978).

Substantial quantities are also used in the rest of the world especially in Canada, Great Britain, USSR, and Western Europe and the consumption of pesticides is spectacularly increasing in Asia, Africa and South America. The wide spread application of pesticides in agriculture, forestry, industry, in and around the home result in contamination of soil, water, air and vegetation. Again, certain pesticides are persistent and application of these chemicals result in the contamination of soil, water air and vegetation. Chemical pesticides are posing a great threat to environment. Yet the benefits derived from their use such as increased food production and prevention of disease in plants represents an equally strong argument for their continued use.

B. History on Pesticides Usage and Pesticides in Vogue:

Ever since the dawn of civilisation man has continually endeavoured to improve his living condition. In his efforts to produce adequate supplies of food, man has been opposed by ravages wrought by insect pests and crop diseases. The use of pesticide is not new. As long ago as 70 A.D. Plinius recommended arsenic as an insecticide. By the 16th century, the Chinese were applying moderate amounts of arsenic compounds as insecticides. In 1763 nicotine was used for the first time, in 1818 extracts of pyrethrum flower, in 1865

parts Green in 1886 hydrogen cyanide, in 1892 lead arsenate, in 1907 calcium arsenate and in 1927 a root extract rotenone were used. The first synthetic insecticide dithiocyanodiethyl ether was used in 1929. Some of these chemicals were relatively persistent and residues of arsenic are still found in soil from use prior to the second world war (Edwards, 1978).

In 1939, Muller discovered the powerful insecticide properties of dichlorodiphenyl trichloro ethane or DDT. From about 1945, several insecticide chlorinated hydrocarbon cyclodiphenyl compounds were introduced though they did not come into widespread use until the Middle (i.e.) 1950 such as aldrin, heptachlor and endrin (Cremlyn, 1978).

Biocidal agricultural chemicals, collectively called pesticides which include the insecticides, fungicides, acaricides, nematocides, herbicides, rodenticides, and molluscicides have proved to be the most effective, dependable, and economical tool in pest management on crops. Use of correct pesticides at the proper stages of crop growth, and at the appropriate time in relation to the pest appearance helps in averting or minimising the losses due to pest attack (Vasanthraj David, 1978).

There is a 15 per cent increase in the consumption of pesticide every year throughout the world. During the

last 10 years the use of DDT alone in India has increased nearly 4 folds. It is estimated that in 1981 DDT requirement alone during 1985-86 would be about. 25000 tonnes which will be twice than that of in 1981. India is importing around 15,286 million tonnes of pesticides every year. The commonly used pesticides in India are Fenitrothion, Malathion, Bromophos, BHS derivatives, toxaphene and other insecticides which are less toxic effects. DDT is also widely used though it has got deleterious toxic effects (Suryanarayana Raju, 1979).

C. Classification of Pesticides:

In common man's language pesticides are substances which are applied to control objectionable insects, weeds and organisms. Pesticides may be defined as agrochemicals designed to combat the attack of various pests on agricultural and horticultural crops. Pesticides are after classified according to the target organisms such as insecticides, fungicides etc., (Nene et al., 1975). Pesticides are classified according to their chemical nature and reported by Nene et al., 1975). is given in figure I.

Algicides Insecticides Hericides Rodenticides Fungicides Nematocides Acaricides

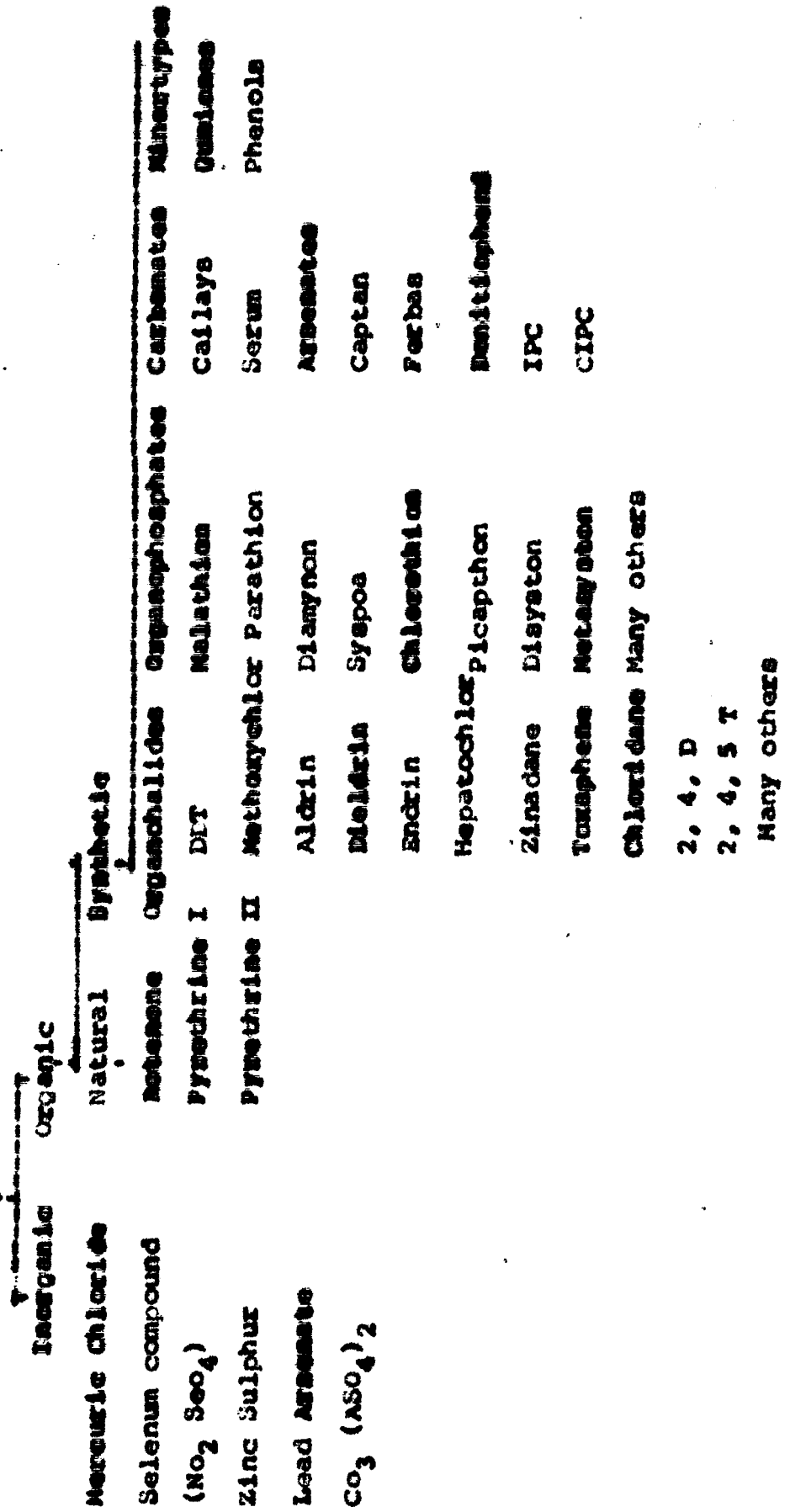


Figure 1
CLASSIFICATION OF PESTICIDES

D. Residual Action of Pesticides:

(1) Some Important Definitions:

a. Acceptable Daily Intake (ADI):

The ADI of a chemical is the daily intake which during an entire life time appears to be without appreciable risk on the basis of all the known facts at the time. It is expressed as mg of chemical as it appears in the diet per kg/body weight/day.

ADI is based on feeding tests on animals over two years and are derived from the highest concentration of the pesticide that gives no discernible effect. The ADI format is established by insisting a safety factor of 100 ADI values which serve as a basis for stipulating residues of pesticides on and in food stuffs.

b. Tolerance:

A tolerance is the maximum concentration of pesticides residue that is permitted in or on food, at a specified stage in harvesting. Storage, marketing or preparation of the food kept the final product of consumption. The consumption is expressed in parts by weight of the pesticide residue from million parts by weight of the food.

C. L.D. 50 Value:

The lethal dosage (mg/kg/body weight) of a chemical which kills 50 per cent of the test animals is called L.D. 50. of the chemical. They vary with age, sex, nutritional status, species, formulation of the chemicals and route of administration. Of necessary L.D.50. values can be applied to man only with reservation.

The toxicity of any materials can be measured in different ways depending on the route by which material enters the body, orally or dermally. Toxicity is expressed in terms of L.D. 50.

(ii) Effects of Pesticide Residue:

The use of pesticide is accompanied by a variety of undesirable environmental effects (Kalva and Chawla, 1981). Since these pesticides and their metabolites are toxic in nature their effect on environment has become a growing concern to everybody. Their residues can cause ecological imbalance and if passed into the food chain, there can be potential health hazard (Agnihotri et al., 1980). The effects include excessive mortality and reduced reproduction potential in organisms such as birds and fishes.

An important aspect of pesticide is the desirability of deposition of persistent residues of the pesticides

for longer lasting control over the pests. But, the residues should not be harmful to the environment and to the nontarget organisms.

The poisoning of chlorinated pesticides especially DDT leads to shivering movements which is followed by convulsions and death. With other chlorinated pesticides, there will be occasional trembling for only a few seconds to several hours. Abnormal postures like keeping the head between the fore legs is seen. Some animals keep their heads pressed against a wall or fence. Continuous chewing is seen with copious flow of thick saliva, froth formation and protrusion of tongue. During the convulsive stage, high fever may also occur. Predominant use of pesticides like DDT in public health is still prevalent for malaria eradication. When mice are subjected to, prolonged exposure to DDT showed an increasing incidence in the succeeding generations. The IARC work revealed that parenchymal liver cell tumours were malignant. In these circumstances, any possible risk to man, as indicated by the animal studies is outweighed by the benefits arising from properly controlled use of DDT (WHO, 1973).

The tissues of the most human beings contain at least small quantities of organo-chlorine residue and

some, particularly individual involved in spray application, contain large amount. Though there are no confirmed deaths of the residues, it is yet to be proved that it is carcinogenic.

E. Pesticide Residue in Water:

Certain pesticides are persistent and application of these chemicals result in the contamination of water resources due to spray drop, direct application, run off resulting from rain fall and irrigation. The main source of this kind of pollution was BHC, DDT and other chlorinated compounds which are relatively more persistent than the organophosphorus pesticides. War against pesticide as water pollutants and fish toxicants has been waged since the early fifties. Many publications are accumulated to show the pesticide contamination in water resources in amounts ranging upto a few parts perbillion (Zwery et al., 1969). On rare occasions, higher concentrations of pesticides appear in portable water, usually as a result of industrial discharge. Pesticides such as BHC (HCCN) toxaphene can impart undesirable taste and odour to water at levels of 5.20 ppb (Rosern, 1959).

Nicholson and co-workers (1962) investigated the run off from a peach orchard into a farm pond. They found

19 ppm of parathion in the mud pond and 0.01 - 1.22 ppb in the water. Tarafwell and Henderson (1956) estimated the dieldrin content of run off water from an area treated with dieldrin at 4.66 lb/acre. The first run off contained 0.13 ppm and the third 0.01 ppm. Heavy mortality in the Mississippi river in the Northern Alabama following heavy rains indicated that the toxic materials were washed from the pesticides treated soil to the stream. Metcalf (1964) analysed water samples from 100 locations in U.S. They ranged in the following order (ppb). Endrin - 0-0.094, Dieldrin - 0 - 0.118, DDT - 0-0.37 and 0.60 - 0.13. Though the levels of pesticides are minute, it can add a significant quantity to the human body along with other sources such as food and air. A report states that the discharges of pesticide residue from the central valley into San Francisco Bay has been estimated to about two tons per year. As shown by Weisloede and Gunther (1966) if one drinks 2 litres of water per day containing 10 ppm of pesticide, one ingests 0.02 g per day. But the drinking water in U S contains 2 ppb and according to national quality net works report the intake of pesticides from this source is something less than 0.004 mg/day.

Ochiai (1969) evaluated the concentration of BHC in rain water and atmosphere after the insecticide was

applied to the ground during rainfall. The results showed that even in urban area where agricultural activity was small, BHC existed in rain water leading to the surmise that there was extensive pollution due to BHC. The high BHC content in rain water during summer rather than winter was considered to have some relationship with the spraying period. But there was no relationship between the BHC concentration and meteorological conditions. Experiments showed that BHC was present in rain water in dissolved state. Analysis conducted by Visweswariah et al., (1973) revealed that the drinking water in ponds located in the coffee estate around Hassan district, Karnataka contains 0.02 - 0.2 ppm of BHC. River pollution with the farm chemical is about 50 times high in Japan as in England. Because of the extensive use of unrefined BHC in agriculture, the accumulation of the beta BHC is said to have chronic toxicity five times the gamma BHC and the accumulation factor in the body fat is comparatively enormous (Janvi, 1972). The pesticide magnification illustrated by these pesticide residues is more than 3000 fold in biological systems. Such level of accumulation in the bodies of animals through food chain may impair co-ordination and behaviour to prevent toxic manifestation.

Cohen and Pinkinton (1966) analysed rain water which contained two pesticides applied previously in an area one mile away from the sampling site. Organic chlorine and sulphur containing compounds were detected. Additional evidence for the finding of organo chlorine pesticides in rain water was provided by Wheatley and Hardman (1965). The data revealed the presence of organo chlorine pesticides in the atmosphere and subsequently in the rain water resulting from the volatilisation of pesticides from the upper surface of pesticide treated soils. The average concentration of format in rain water sample collected over one month during the period of Nov. 1964 to February 1965 for BHC, for dieldrin 20, and for p - p' DDT 3 parts per 10^{12} parts of rain water, whereas the samples collected only during the periods of rainfall in January and March 1965 averaged 29 and 3 parts per 10^{12} parts of rain water respectively. The conclusion made by Werhis (1965) with similar findings amply justify that agricultural chemicals are continuously contaminating the entire atmosphere. It is reported that the average amount of DDT and its analogues in rain water from seven widely spread stations in rural areas all around the year was 7.9 in 10^{11} ranging from 1.2 to 2.1 in 10^{11} (Lee Lung, 1972). The survey conducted by

Raju et al., (1982) has revealed the following amounts of pesticides residue in water samples BHC - 1 to 2.360 ppb, methyl parathion 0-13000 ppb DDT - 2100 ppb. Tripathi (1966) studied 5 samples of water but could not detect DDT in any of them. According to a government of India's report (1967) the discharge from the Hindustan Insecticide Factory manufacturing DDT at Delhi was suspected to have caused the destruction of fish in Yamuna river. There are reports that cattle and even tiger are dying due to pesticide poisoning.

F. Pesticide Residue in Foods:

The greatest exposure to pesticides, of most consumers, in the general public result from pesticide residue in food (Key Hill, 1969). Pesticide residue in food have therefore been a matter of major concern. Nevertheless, it is very difficult to produce crops that contain no pesticide residues without serious loss due to pests. Milk and meat are also contaminated through the ingestion of contaminated feed by domestic animals. It is imperative that food commodities meant for human consumption should not contain pesticide residues of levels hazardous to human health. In order to regulate pesticide residue to safe levels the Joint Meeting of Pesticide

Residues (JMPR) of FAO/WHO of the United Nations have laid down principles of arriving at the maximum residue limits of pesticides in the food commodities (FAO, 1978). The levels of intake which is considered safe for human even if consumed for their whole life is determined by trials in animals. The ADI and residue level are taken into consideration for establishing maximum residue limits.

1. Pesticide Residue in Grains:

Certain cereals and pulses were analysed in different parts of the country. It is well known that pesticide contamination of cereals and pulses is quite wide spread. In Andhra Pradesh, Hyderabad, 47 of the 77 samples of cereals contained either DDT or BHC residues. Certain samples of rice and pulses also contained residues of organo chlorine insecticide. In all the 16 samples these exceeded the tolerances.

Seventeen of the 54 samples of wheat collected from Punjab contained DDT and 4 contained BHC. The samples from Pantnagar contained DDT. In Delhi, 150 wheat samples were collected during 1965, out of which 13 samples showed BHC residue ranging from 0.07 to 7.0 ppm. In other samples, the presence of BHC and DDT limits were

lower than 0.05 ppm. At Mysore, the seed samples of wheat, maize, sorghum and bajra from different places was found to be contaminated, invariably with very high levels of DDT, BHC and captan. Three hundred and ninety three samples of imported wheat were studied for residue at CFTRI and it was found to contain Malathion at 0.025 to 3.56 ppm. levels (i.e.) below the international tolerance level of 8 ppm. Studies at Punjab Agricultural University, Ludhiana showed that 20 wheat samples from FCI godowns contained malathion residues (Bindra, 1971).

The survey conducted by Majumder (1963) on green gram, bengal gram, black gram, cow pea, field bean, horse gram, mung dhal wheat, jowar, rice and potatoes suspected for insecticide contamination from Mysore, Coimbatore, Pollachi, Erode, Karur, Mangalore were collected over a period of five years and analysed for BHC, DDT and Malathion.

The suspected samples drawn from different market centres in India showed non analysis insecticidal contamination in them. Results showed that the contamination with BHC was commonly noticed in the case of cereals and pulses. Malathion residues were present in many of the wheat samples. In many cases, it was noticed that DDT and BHC were present much more than the permissible limits (Viswesvariah et al., 1975).

Surveys has been made in different countries on the pesticide residue of some of the chlorinated hydrocarbon such as DDT, dieldrin (Cummings and Duggan, 1965). In India, some data on the residues are available in raw cereals, foods, seeds and animal products. It may be seen that suspected samples did contain a high amount of pesticide residue (Majumder, 1973).

The Thacher Committee's report gives data on pesticides contamination of pulses, rice, wheat and flour. (Bindra, 1971). The study carried out at Hyderabad revealed that 14 per cent of the 38 market samples of cereal and ceral products were contaminated. The contaminants were as follows : DDT - 0.25 to 1.0 ppm; BHC traces lindane upto 0.4 ppm. and endrin upto 1 ppm. In the survey conducted at Ludhiana, 12 of the 29 samples of wheat were found to contain DDT and BHC. At Pantnagar all the 15 samples of edible grain contained the DDT residue ranging upto 0.996 ppm and the average being 0.41 ± 0.23 ppm. Thus, the contamination of cereals and pulses and their products appear to be the most important source of pesticide ingested by average Indian.

2. Pesticide Residue in Fruits and Vegetables:

In India, the magnitude of pesticide residues in foods is increasing gradually with hazardous side efforts.

Agnihotri et al., (1974a, 1974b) studied the residues of pesticides in vegetables. It was observed that while most samples contained both the toxicants, more than 25 per cent of the samples showed concentrations either close to or above the tolerance limits. A few samples contained more than 50 ppm, BHC. Jain and Gupta (1976) sprayed brinjal with 0.01 per cent lindane solution at 350 l/ha and analysed the fruits by bioassay for its residue at different intervals. The initial deposit of lindane on fruits was in the range of 10 - 11 ppm which decreased to levels below the tolerance limits in 5 days. During a seven year period, Lakshminarayana and Menon (1975) found that a large number of food stuffs of Hyderabad market including vegetables and fruits contained residues of DDT and BHC in addition to the other pesticides. Out of 1316 samples tested 655 samples contained DDT and 235 samples had BHC, many of which exceed the BHC tolerance limits.

In a series of experiments conducted over three years under two different soil and agroclimatic condition of Udaipur and Johar on carrot, raddish and beetroot, Srivatsava and Kavadia (1976) observed that soil incorporation of BHC at rates 5, 15 and 30 kg.ai/hectare before sowing the root crops resulted in an increased absorption

of the toxicant by the crops on sandy loam soil than on clay loam. Carrot absorbed maximum insecticide followed by raddish and beetroot. Satpathy et al., (1974) studied residues of diazinon in brinjal and cowpea resulting from its soil application in the form of granules. The residues were less than the tolerance limits although diazinon was detected 10 days after treatment. The granular application of disulphur at 2 kg ai/ha to brinjal and cowpea were observed to result in plant residues usually higher than the FDA tolerance unit 0.75 ppm till 3 weeks after application in fruits of both crops.

Hameed and Ratanlal (1971) investigated the residues of malathion on cabbage, cauliflower and Knol-khol after treating the crops in the form of EC, WDP and dust formulation using both chemical and bioassay methods. Deposit on cauliflower and other portions of knol-khol were lower than that in foliage. The EC formulation left slightly higher residue than the WDP or dust but the residues of WDP formulation were more persistent than others.

Most of the data on pesticide residue in market samples of vegetables are from Hyderabad, Ludhiana and Mysore. Of the 727 samples analysed, as many as 514 samples (i.e) 71 per cent were found to contain pesticides.

At Mysore all the 300 samples of leafy vegetables contained pesticides and in many samples the levels exceeded the tolerance limits set by the FDA of USA. The vegetables found contaminated were beans, bhindi, brinjal, cabbage, carrot, potato and tomato. The pesticides detected were aldrin BHC, Chlordane, DDT, endrin, heptachlor and lindane. DDT was met within all the contaminated samples except six of them. It has been found in fresh potatoes at levels upto 8.9 ppm. At Ludhiana 4 of the 10 brinjal samples contained DDT while 6 of the 8 samples contained of bhindi from different markets in Punjab contained aldrin. It may be noted that this pesticides has been detected in bhindi, brinjal, cabbage, carrot and potato at Hyderabad. It was found that among 44 grape samples, 6 contained malathion, while 30 others contained methyl parathion and parathion. In some samples methyl parathion residues exceeded the tolerance limit. Only 2 of the 10 vegetables sample taken from Pantnagar market had DDT residues. The maximum residues was 0.72 ppm. In Punjab, Shalla et al., (1971) found 6 of the 8 market samples of bhindi to be contaminated with endrin, the residues being upto 0.38 ppm. Jaglan and Chopra (1970) studied 10 market samples of brinjal and tomato at Ludhiana and detected DDT in 3 brinjal samples and one tomato

sample, the residues being 0.08 ppm. in tomato and 0.08 to 0.8 ppm in brinjal. A review by Agnihotri and Mithyandi (1978) reveals the quantity of the pesticide residue in plants, fruits and vegetables.

Duggan and Dawson (1967) have shown that the average US diet contained chlorinated hydrocarbon residues distributed in the following order. Dairy products contributed 17.5 per cent, meat, fish, poultry 35 per cent, grain and cereal 7.5 potatoes 1.3 per cent leafy vegetables 2.5 per cent.

3. Pesticide Residues in Foods After Cooking:

The residual effect of the pesticides is generally found to be decreased after processing. Wheat samples were fertifed with fenitrothion and methyl parathion and they were milled. Fenitrothion was mostly present in the bran, and a small amount in the endosperm of flour. It was found that the high reduction in the insecticide content is due to the volatalisation and breakdown of insecticide during milling (Viswesvariah et al., 1983).

Grapes and vegetables like bean, tomato cauliflower, cabbage, lady's finger, brinjal and palak which

are free from the pesticide residue were selected and were fortified with lindane, BHC, and X-factor. The decontaminating agents studied were cold water wash, hot water wash, 2 per cent acetic acid in water, 2 per cent sodium bicarbonate and 1 per cent ethanol. It was found that the pesticide residue was reduced by ninety per cent when treated with ethanol. In general, the degree of removal of lindane was more in all the vegetables with different chemical solution, compared to factor and BHC (Raju *et al.*, 1983).

Experimental Procedure

III EXPERIMENTAL PROCEDURE

Experimental procedure involved in the conduct of this study on Pesticide Residue in selected market samples of cereals and pulses and impact of cooking is described as follows:

- A. Selection of the cereals and pulses
- B. Identification of Pesticide Residues to be analysed
- C. Analysis of Pesticide Residue

A. Selection of Cereals and Pulses:

Most commonly consumed staple cereals namely rice, wheat, sorghum and ragi were selected for pesticide residue analysis as these are the main stay of the diets of the population groups in and around Coimbatore and hence would throw light on the degree of contamination of these daily consumed cereals due to pesticide residue. This information would be of great value as it would give an idea of the possible cumulative degree of pesticide ingestion by the common man. For the same reason four commonly consumed pulses namely green gram dhal, black gram dhal, Bengal gram dhal and redgram dhal were also selected for their pesticide residue analysis.

For the collection of all the above cereals and pulses, three main markets of Coimbatore in the areas of Gandhipuram,

North Colabatore and Town Hall were identified and from each market three samples for each of the cereal and pulse grains sampled. These samples were randomly collected from the shops in the market area and the procedure outlined in CFTRI Manual (1978) for Pesticide Residue Analysis adhered to. The collected samples were then stored in sterile containers before analysis.

A portion of the collected sample was subjected to boiling as the method of cooking before analysis. This was done because it was thought of interest to see if any pesticidal residue was lost due to ordinary household cooking methods. It was hoped that such information would further bring to light the possible minimal pesticide residue in the actual foods consumed as more of the cereals and pulses are invariably cooked before eating. Hence, apart from the market samples as purchased for the four cereals and pulses, all the samples were analysed for pesticide residue after cooking as well. Since boiling for 20 minutes in hot water was found to be the ideal cooking time for most of the cereals and pulses, all the samples were boiled for 20 minutes in hot water uniformly before analysis.

B. Identification of Pesticide Residue to be Analysed:

The most commonly used pesticides on cereals and pulses crops are organochlorine and organophosphorus compounds

(Visweswaraiiah et al., 1978). Hence the possibility of pesticide residues that could be encountered in the cereals and pulses as it comes for consumption in the market would be those of the above compounds. The residual compounds that might possibly be present in the cereals and pulses, would then thus be organochlorine residues like Dichloro Dimethyl Trichloroethane (DDT), Dichloro Dimethyl Ethane (DDE), benzene hexachloride (BHC) and organophosphorus residue like malathion. Carbanate is another common residue found in foods in general. Hence, all the samples collected were subjected to analysis for the above residues using thin layer chromatography and quantification by gas liquid chromatography procedure (Visweswaraiiah et al., 1972).

C. Analysis the Pesticide Residue:

Pesticide residue analysis consisted of the following main steps.

1. Purification of the chemicals,
2. Extraction and clean-up of the samples,
3. Detection of the pesticide residue, and
4. Quantification of the pesticide residue.

1. Purification of the chemicals:

As per the procedure outlined in the CFTRI Manual (1978) all the chemicals were purified before it could be used for analysis. The details of the procedure for cleaning the chemicals is presented in Appendix I.

2. Extraction and Clean up of the samples:

One hundred grams of the sample both raw and cooked were taken in replicates, for analysis and the extraction and clean up procedure followed as per the CFTRI procedure (1978) for pesticide residue analysis. The details for extraction and clean up and ingestion into the column for complete elution is given in Appendix II.

3. Detection of Pesticides Residues:

Detection of the pesticide residues were done by plating the eluted sample on thin layer chromatographic plates and the details of the procedure as per CFTRI Manual (1978) is given in Appendix III.

4. Quantification of the Pesticide Residues:

The quantification of the pesticide residue was done by gas-liquid chromatography by injecting a column with the sample concentrates. The peaks from the graph were quantified as per standard procedure and compared with standards to obtain actual quantity of each pesticide. Details of quantification is given in Appendix IV.

Results and Discussion



IV RESULTS AND DISCUSSION

Results of this investigation on 'Pesticide Residue in selected market sample of cereals and pulses and impact of cooking are presented and discussed under the following headings:

A. Pesticide Residue in Cereals as Purchased and after Cooking.

1. Dichloro Dimethyl Trichloroethane (DDT) residue
2. Dichloro Dimethyl Ethane (DDE) Residue
3. Benzene Hexachloride (BHC) residue
4. Malathion Residue
5. Percentage decrease of pesticide residue in cereals due to cooking.

B. Pesticide Residue in Pulses as Purchased and after Cooking.

1. Dichloro Dimethyl Trichloroethane (DDT) Residue
2. Dichloro Dimethyl Ethane (DDE) Residue
3. Benzene Hexachloride (BHC) Residue
4. Malathion Residue
5. Percentage Decrease of Pesticide Residue in Pulses Due to Cooking

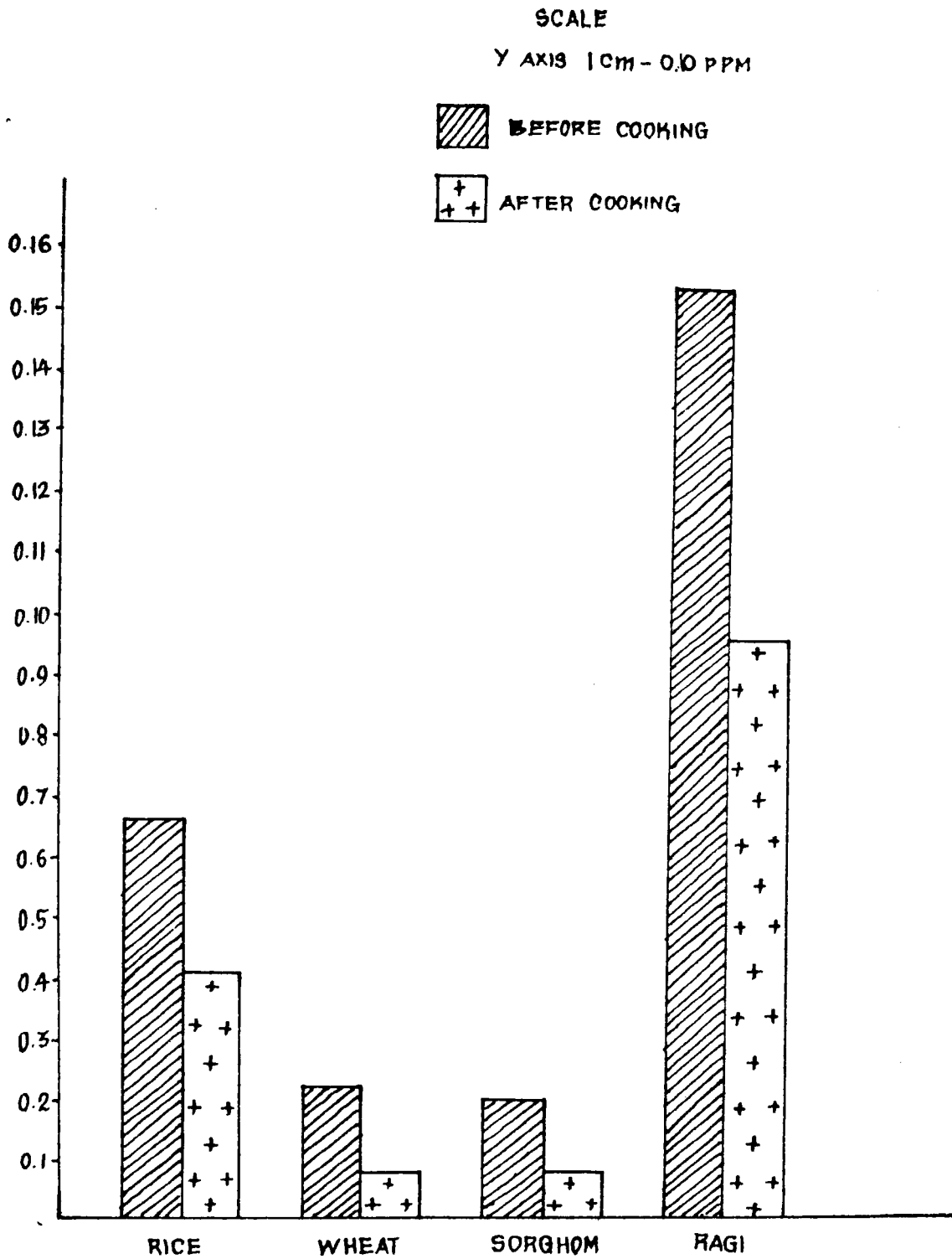
A. Pesticide Residue in Cereals as Purchased and After Cooking:

Insecticides or pesticides are applied to cereal grains to prevent loss due to infestation during cultivation. Since

most of these are topically applied or sprayed even after harvest, residues are bound to be present when they are ready for consumption as available in the market. In order to assess the pesticidal residue in cereals, four commonly consumed cereals namely rice, wheat, sorghum and ragi were sampled from three different market sources in Coimbatore in triplicates. The most common residues from the pesticides are DDT, DDE, DDC and Malathion. Hence, these residues were analysed in all the thirty six samples, collected as purchased. All the thirty-six samples were subjected to cooking by boiling method and residues of the above pesticides analysed again. All the samples were analysed for carbamate residue and it was found totally absent in all the cereals and pulses.

1. Dichloro Dimethyl Trichloro Ethane (DDT) Residue:

DDT is one of the most common chemical component of pesticides and is a favourite among cultivators to save the cereal grain. It has also been reported by Lakshminarayana (1980) that DDT is one of the frequently encountered contaminant residue in foods. The market samples of the four cereals were analysed for DDT residue and the results on its presence in both raw and cooked samples of cereals is presented in Table I and Figure 2. The individual values obtained is given in Appendix V.



DDT RESIDUE AS PURCHASED AND AFTER COOKING IN CEREALS.

Figure:2

TABLE I
DDT RESIDUE IN RAW AND COOKED CEREALS

Market Source	Rice		Wheat		Sorghum		Ragi	
	BC†	AC**	BC	AC	BC	AC	BC	AC
1	0.090	0.072	0.006	0.002	ND	ND	0.420	0.270
2	0.039	0.007	0.030	0.010	ND	ND	0.030	0.013
3	ND*	ND	0.030	0.009	0.02	0.008	0.010	0.002
Mean	0.0645	0.0395	0.022	0.007	0.02	0.008	0.153	0.095

† Before Cooking ; ** After Cooking

*ND - Not Detectable

Pesticide residue of DDT was present in almost all samples of cereals except in one sample collected from source III in rice, and two samples of Sorghum (Sources I and II). On an average 0.0645 ppm of DDT residue was present in rice, 0.022 ppm in wheat, 0.02 in the only one sample sorghum in which DDT was detected and 0.153 ppm in ragi was purchased from the market. On cooking, in all the cereals, DDT residue showed considerable decrease. After cooking, it was 0.0395 ppm in rice, 0.007 ppm in wheat, 0.008 in the single sample of sorghum and 0.095 in ragi.

The tolerance limit for DDT as recommended by (FAO/WHO 1973), is 0.78 ppm and it is notable that none of the cereal

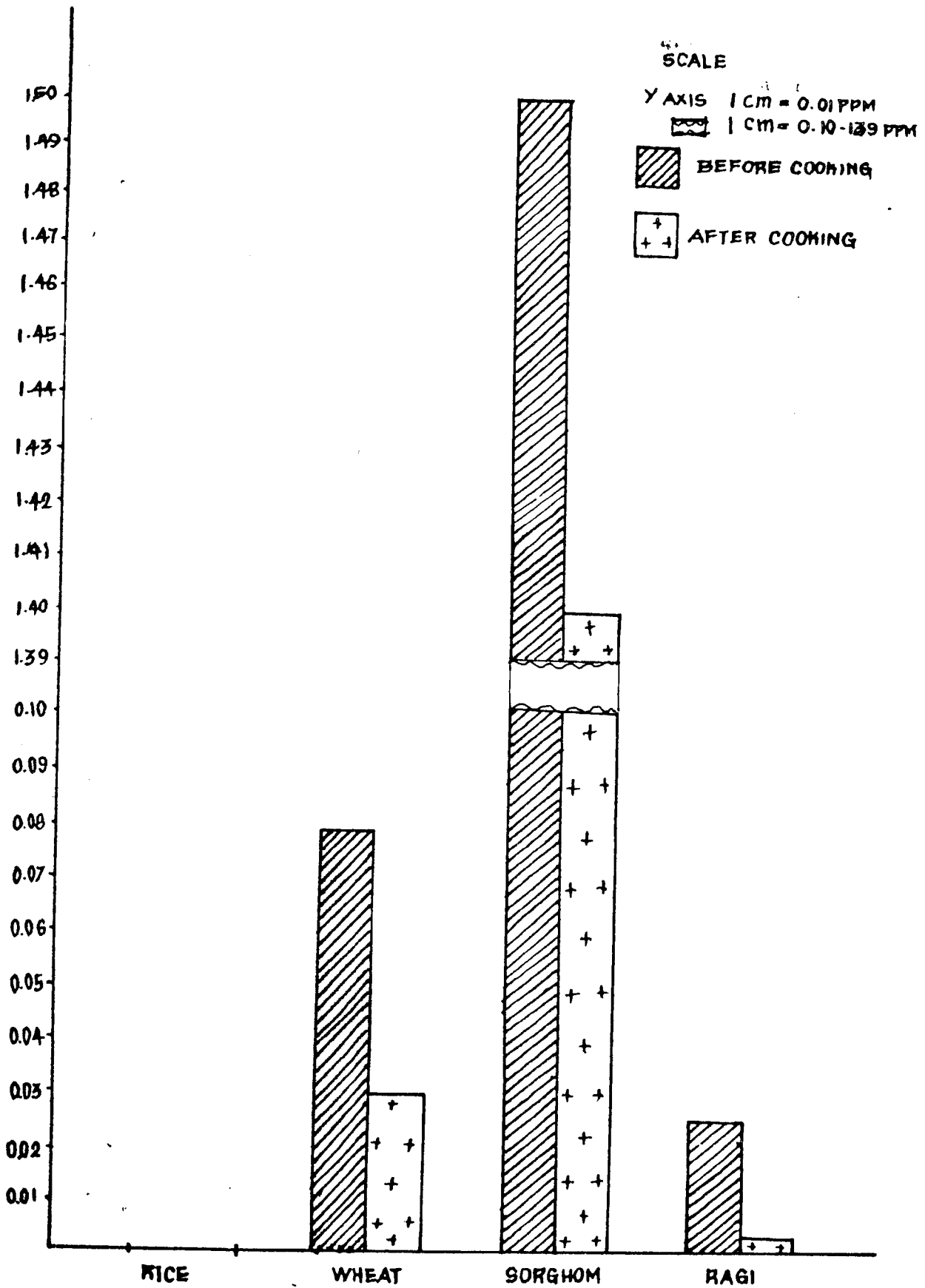
grains collected from the market had values nearer to the tolerance limit. The fact that cooking further reduced the DDT residue is encouraging and with the available knowledge on tolerance limits of pesticides, may be the current results indicate that the cereal grains as purchased from the market is not harmfully contaminated with DDT although traces are present even after cooking. Long term effect of these residues on individuals however is not known.

2. Dichloro Dimethyl Ethane (DDE) Residue:

Table II and Figure 3 gives the DDE residue in the cereal grains studied both as purchased and after cooking. Individual values as per Appendix V.

TABLE II
DICHLORO DIMETHYL ETHANE (DDE) RESIDUE IN CEREALS

Market source	Rice		Wheat		Sorghum		Ragi	
	BC	AC	BC	AC	BC	AC	BC	AC
1	ND	ND	0.08	0.03	3.00	2.700	ND	ND
2	ND	ND	ND	ND	ND	ND	0.0012	ND
3	ND	ND	ND	ND	0.010	0.003	0.050	0.0030
Mean	ND	ND	0.08	0.03	1.5	1.35	0.0251	0.0015



DDE RESIDUE AS PURCHASED AND AFTER COOKING IN CEREALS

Figure: 5

DDE residue was not detectable in the rice samples, two wheat samples and one each of sorghum and ragi samples, indicating that this DDE is not probably a common residue encountered in cereal grains. In one of the samples of wheat 0.08 ppm of DDE, was present as purchased which reduced to 0.03 ppm on cooking. In sorghum, on an average 1.5 ppm of DDE was present and it was reduced to 1.35 ppm on cooking. It is notable that 0.78 ppm is the tolerance limit and one sample of sorghum contained about three times the tolerance level even after cooking. This needs consideration and attention as it is not possible for the ordinary consumer to know the residual content when he purchases and often choice of market for purchase cannot be predicted. Moreover DDE is the reduced form of DDT, it is notable that the presence of DDE in one of the samples of Sorghum is one the same market sample as the one in which DDT is not detectable. This would mean then, that in this market sample, that organo chlorine residue is quite high and is a matter worth receiving attention from health authorities. In the case of ragi, DDE residue as purchased was 0.0251 ppm which reduced to 0.0015 ppm on cooking. These results indicate that in general DDE residue is rather low in content in cereal grains and is much below the tolerance limit of 0.78 ppm except for one market sample of sorghum.

3. Benzene Hexachloride (BHC) Residue:

Another important organochlorine residue commonly encountered is BHC residue. BHC residual analysis on the four cereals as purchased and after cooking is given in Table III and Figure 4. Individual Values for each sample analysed is given Appendix V.

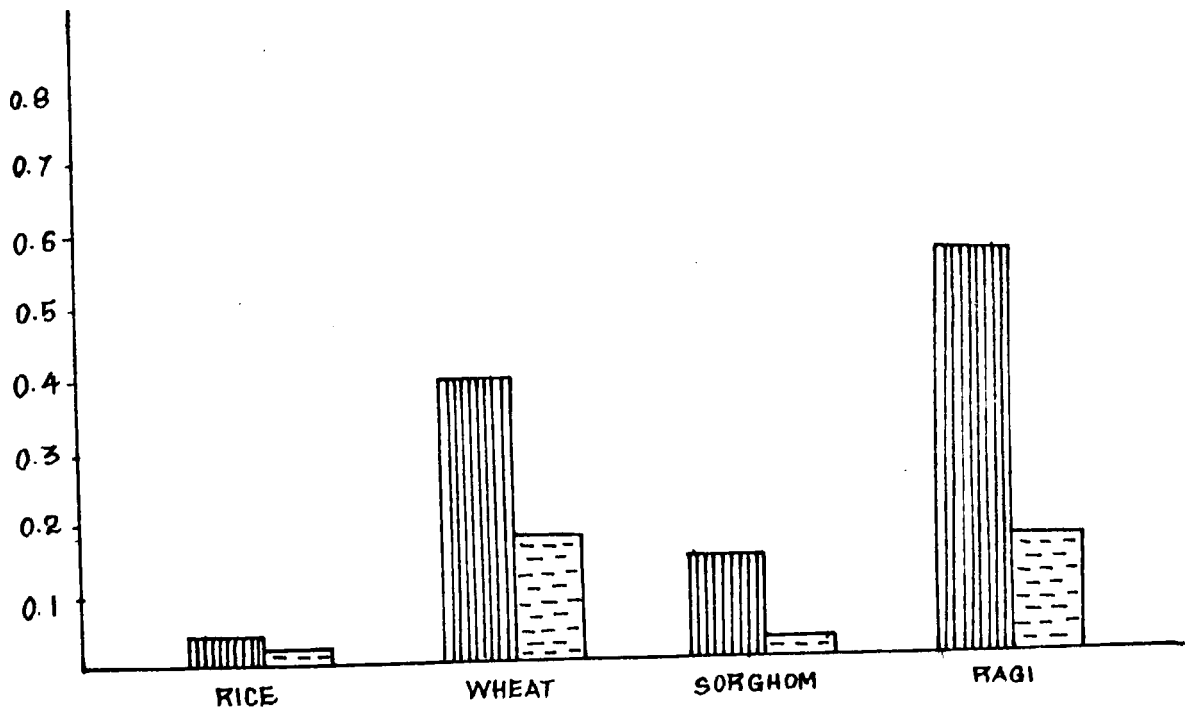
TABLE III
BENZENE HEXACHLORIDE (BHC) RESIDUES IN
CEREALS

Market Source	Rice		Wheat		Sorghum		Ragi	
	BC	AC	BC	AC	BC	AC	BC	AC
1	0.06	0.03	0.46	0.090	0.07	0.020	0.70	0.250
2	0.01	0	0.07	0.001	ND	ND	0.38	0.0130
3	0.01	0	0.66	0.43	0.2	0.012	0.62	0.220
Mean	0.026	0.01	0.39	0.17	0.13	0.016	0.566	0.161

Except for one sample of sorghum, all other samples of all the four cereal grains contained BHC residue. On an average rice samples had 0.026 ppm BHC residue as purchased which reduced to 0.01 ppm after cooking. The residue was 0.39 ppm in wheat as purchased which reduced to 0.17 ppm

SCALE
Y AXIS 1 CM = 0.1 PPM

BEFORE COOKING
AFTER COOKING



BHC RESIDUE AS PURCHASED AND AFTER COOKING IN CEREALS

Figure : 4

after cooking. In the two samples of sorghum, BHC residue was 0.13 ppm as purchased, which reduced to 0.016 ppm after cooking. In ragi, the BHC residue was 0.546 ppm in the market sample and it reduced to 0.161 ppm after cooking. The tolerance limit for BHC is 0.25 ppm as recommended by (FAO/WHO, 1973). Both ragi and wheat samples as purchased has BHC residues above the tolerance limits but it is reduced below the tolerance limit on cooking. Although it is a factor to be considered, from the point of view of health, the market sample of some cereal grains do contain residues of organo chlorine compounds above the tolerance limit reduced almost and in general cereals are cooked before eating.

4. Malathion Residue:

Malathion, has been extensively used as an effective and suitable insecticide for cereal grains (Moorthy and Srivatsava, 1978). Hence the possibility of all samples of cereal grains sprayed with Malathion. The residue of organophosphorus insecticide in the four selected cereal grain as purchased and after cooking was analysed and the data is presented in Table IV. Individual values as per Appendix V.

TABLE IV
MALATHION RESIDUE IN CEREALS

Market Source	Rice		Wheat		Sorghum		Ragi	
	BC	AC	BC	AC	BC	AC	BC	AC
1	ND	ND	ND	ND	0.007	0.002	ND	ND
2	0.002	0	ND	ND	0.03	0.023	0.008	0
3	ND	ND	ND	ND	ND	ND	ND	ND
Mean	0.002	0	ND	ND	0.0185	0.0125	0.003	0

It is notable that none of the wheat samples had any detectable effect of Malathion residue. Only one sample each of rice and ragi and two samples of sorghum have residues of Malathion. It may be observed that the malathion residue in the single rice sample was only 0.002 ppm as purchased which reduced to nil after cooking. In the case of ragi it was 0.003 ppm as purchased which again reduced to nil on cooking. In the case of sorghum, on an average 0.018 ppm of Malathion was encountered in the market sample which was reduced to 0.012 ppm in the cooked sample. Malathion has a recommended tolerance limit of 4.0 ppm (FAO/WHO, 1973). None of the sample analysed had any perceivable malathion residue.

5. Percentage decrease of pesticide residue in cereals due to cooking:

The percentage decrease of pesticide residue in cereals after cooking is tabulated in Table V.

TABLE V
PERCENTAGE DECREASE OF PESTICIDE RESIDUE IN CEREALS
DUE TO COOKING

Pesticide Residue of	Rice	Wheat	Sorghum	Ragi
DDT	38.7	68.18	60.0	37.9
DDE	ND	62.5	10.0	94.0
BHC	61.53	56.41	87.6	71.5
Malathion	100	ND	32.4	100

The percentage loss of DDT residue in cereal grains ranged from 37.9 per cent to 68.18 per cent. The rice sample analysed had the minimum loss. The DDE residue loss ranged from 10 per cent to 94 per cent and this was not detected in the rice sample. The percentage loss of BHC residue ranged from 56.41 per cent to 87.6 per cent.

The Malathion residues present in the two samples were completely removed after cooking and the malathion was the only residue which was removed cent per cent after cooking.

B. Pesticide Residue in Pulses as Purchased and After Cooking

Sample of four commonly used pulses namely greengram dhal, black gram dhal, Bengalgram dhal and red gram dhal were collected from three different market sources in triplicate and analysed for pesticide residues.



1. Dichloro Dimethyl Trichloroethane [DDT] residues

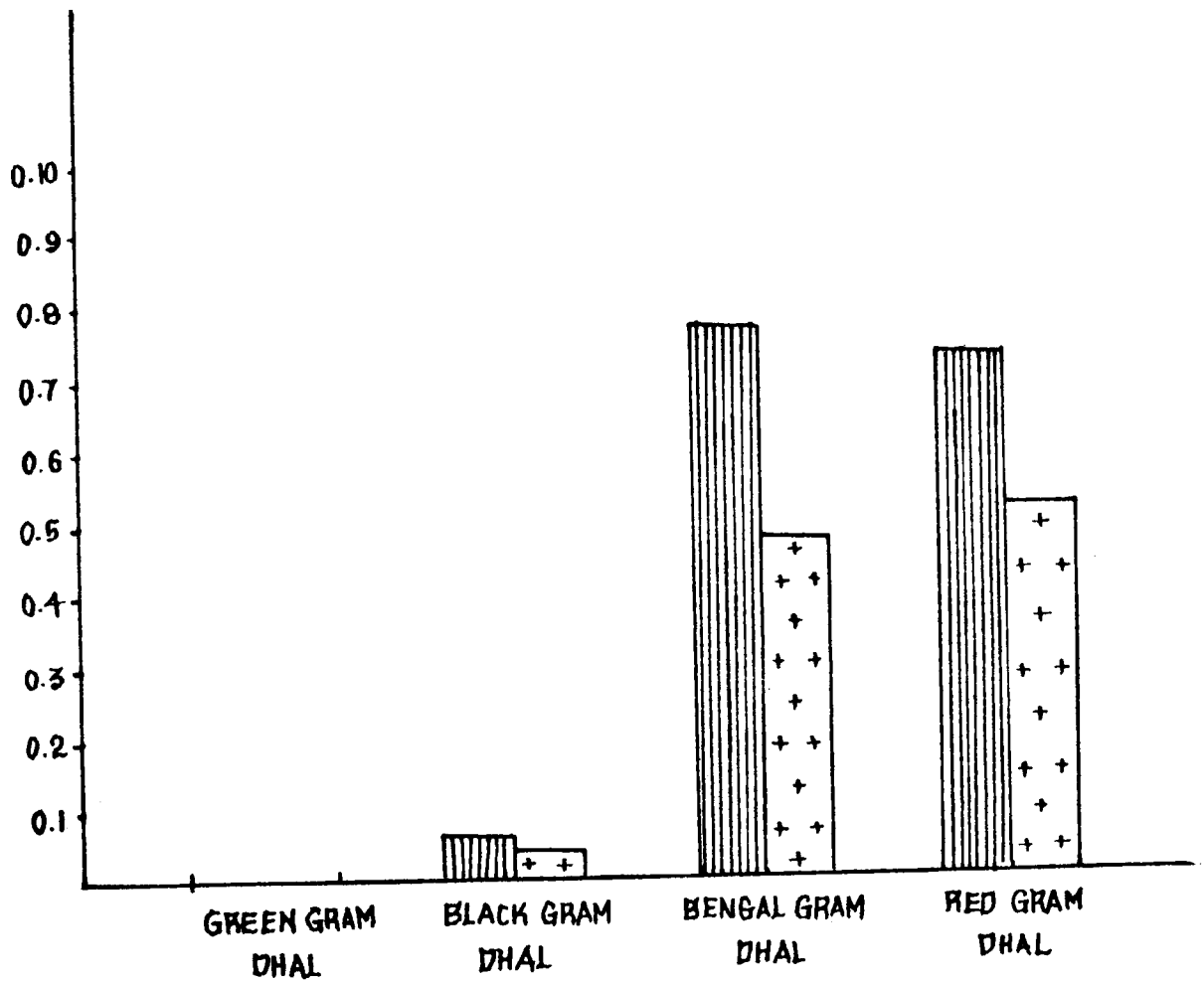
Residues of DDT as analysed in the four pulse samples as purchased and after cooking is given in Table VI and in Figure 5. Details of individual value is given in Appendix V.

TABLE VI
DICHLORO DIMETHYL TRICHLOROETHANE (DDT) RESIDUES IN PULSES

Market source	Greengram Dhal		Blackgram Dhal		Bengalgram Dhal		Redgram Dhal	
	BC	AC	BC	AC	BC	AC	BC	AC
1	ND	ND	0.007	0.006	1.000	0.90	ND	ND
2	ND	ND	0.010	0.007	ND	ND	0.66	0.430
3	ND	ND	0.097	0.082	0.490	0.017	0.79	0.620
Mean	ND	ND	0.038	0.031	0.745	0.458	0.725	0.528

SCALE
Y AXIS 1 CM = 0.1 PPM

 BEFORE COOKING
 AFTER COOKING



DDT RESIDUE AS PURCHASED AND AFTER COOKING IN PULSES

Figure: 5

Greengram dhal collected from the three sources did not contain any DDT residue. Two samples each of Bengal Gram and Red Gram Dhal contained DDT residue whereas all the samples of Black gram dhal had a pesticide residue. On an average, DDT residue of blackgram dhal before cooking was 0.033 ppm and was reduced to 0.031 ppm after cooking. In the case of Bengal Gram Dhal, DDT residue of 0.745 ppm was observed in the market samples which was reduced to 0.458 ppm on cooking. In the case of red gram dhal of 0.725 ppm was the DDT residue observed in the market sample which was reduced to 0.525 ppm on cooking. The acceptable tolerance limit according to FAO/WHO (1973) is 0.78 ppm for DDT. Except for one market sample of Bengal Gram dhal and one of red gram dhal, none of the other samples had DDT residue level higher than the tolerance limit. The higher DDT residue level of one sample of Bengal Gram Dhal was 1.0 ppm which was reduced to only 0.9 ppm on cooking, which again is not a safe limit. From the point of view, such samples need consideration from the health authorities. The single market sample of red gram dhal which had a value of 0.72 ppm of residue as purchased reduced to 0.62 ppm on cooking with the consolation that it is less than the tolerance level after cooking. Though single instances, these values call attention to the fact that there is need to control market samples in order to minimise the harmful effect of pesticides.

2. Dichloro Dimethyl Ethane (DDE) Residue:



The DDE residue of the four pulse samples before and after cooking is presented in Table VII and in Figure 6. Details are presented in Appendix 3.

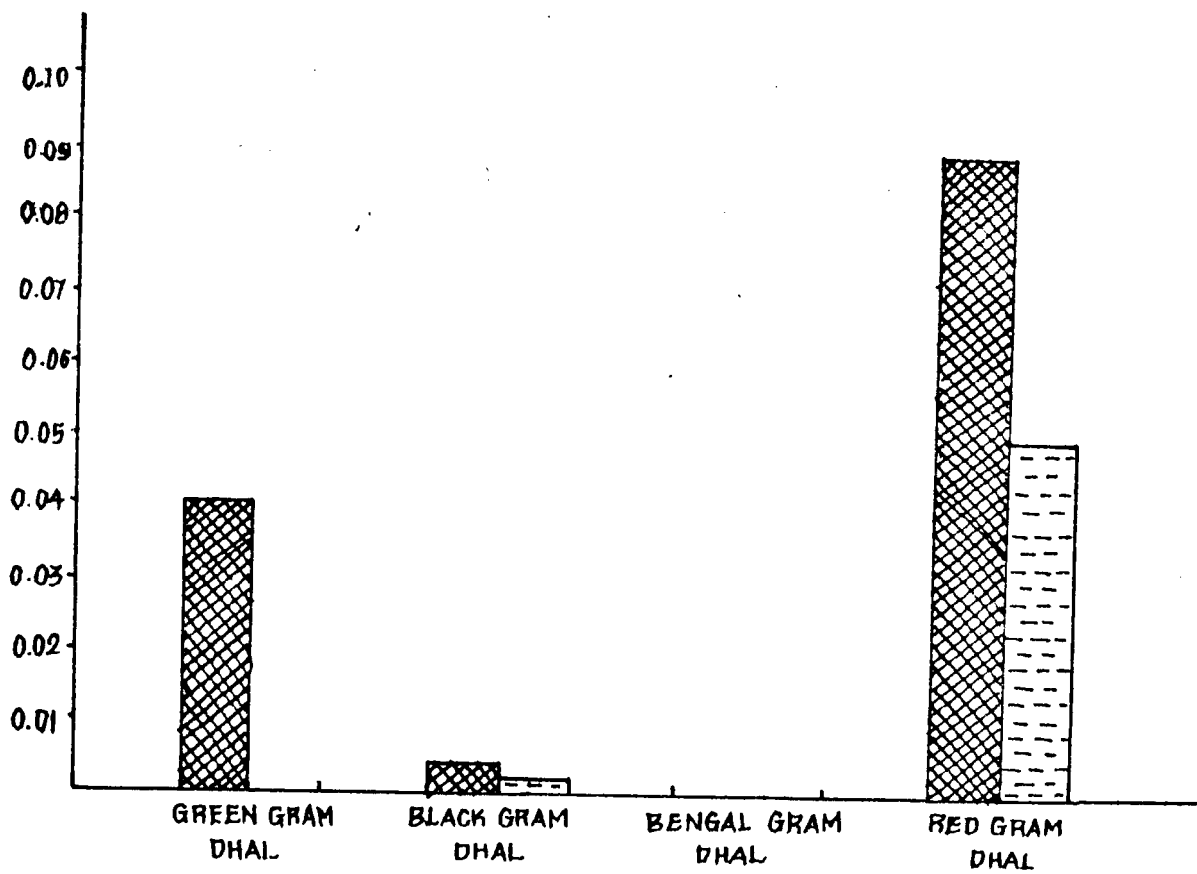
TABLE VII
DICHLORODIMETHYL ETHANE RESIDUE IN PULSES

Market source	Green gram dhal		Black gram dhal		Bengalgram dhal		Redgram dhal	
	BC	AC	BC	AC	BC	AC	BC	AC
1	ND	ND	ND	ND	ND	ND	0.09	0.05
2	ND	ND	0.003	0.0019	ND	ND	ND	ND
3	0.04	0	ND	ND	ND	ND	ND	ND
Mean	0.04	0	0.003	0.0019	ND	ND	0.09	0.05

In the case of greengram dhal only one sample had DDE residue of 0.04 ppm which was reduced to zero on cooking. For black gram dhal only one sample had DDE value 0.003 ppm as purchased which was reduced to 0.0019 ppm on cooking. None of the Bengal gram dhal samples had DDE residue. One red gram dhal sample which did not have any DDT residue, had a DDE

SCALE
Y AXIS CM = 0.01 PPM

 BEFORE COOKING
 AFTER COOKING



DDE RESIDUE AS PURCHASED AND AFTER COOKING IN PULSES

Figure: 6

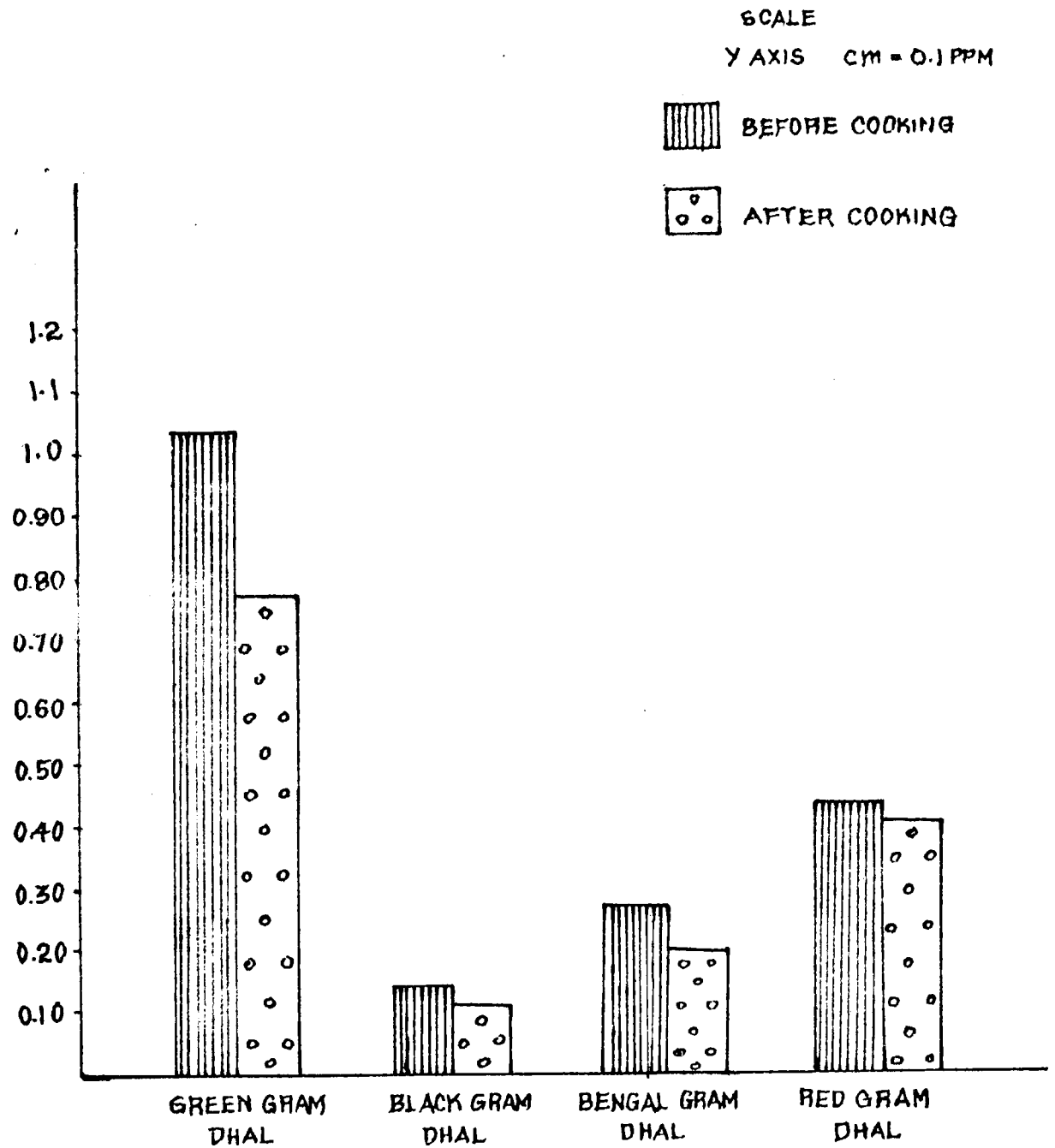
residue of 0.09 ppm before cooking which came down to 0.05 ppm after cooking. As discussed earlier for cereals, DDE is the reduced form of DDT and in some cases like one red gram dhal sample and green gram dhal sample, though DDT residue was not present, DDE residue could be traced in the same samples indicating atleast some organo chlorine pesticide residue. It may however be pointed out that in none of the samples, DDE residue were any where near the tolerance level of 0.78 ppm.

3. Benzene Hexachloride (BHC) Residue on Pulses:

BHC residue of the four pulses as purchased and after cooking is presented in Table VIII and in Figure 7. The details of individual values is given in Appendix V.

TABLE VIII
BENZENE HEXACHLORIDE RESIDUES IN PULSES

Market source	Greengram dhal		Blackgram dhal		Bengalgram dhal		Redgram dhal	
1	2.20	1.72	0.06	0.059	0.03	0.01	0.05	0.04
2	0.17	0.09	0.20	0.170	0.72	0.53	0.82	0.80
3	0.72	0.53	ND	ND	0.07	0.06	0.40	0.38
Mean	1.03	0.78	0.13	0.1145	0.27	0.20	0.42	0.406



BHC RESIDUE AS PURCHASED AND AFTER COOKING
IN PULSES

Figure:7

Except for one sample, both the greengram dhal samples had a value higher than the tolerance level of BHC (0.25ppm) on an average, in the three sources, the BHC residue was 1.03 ppm before cooking which reduced to 0.78 ppm after cooking. All these value were higher than the tolerance value. In the case of black gram dhal, one of the sources did not have any detectable amount of BHC. Among the other two samples, one sample had a value of 0.06 ppm before cooking which was not considerably reduced even after cooking (0.059 ppm). The third sample had a value of 0.20 ppm which was reduced to 0.17 ppm after cooking. However, on an average black gram dhal contained BHC residue within the tolerance limit. In the case of Bengalgram dhal, one market sample had a value above the tolerance limit thus making the average value from the three markets to 0.27 ppm a value slightly above the tolerance limit of 0.25 ppm. On cooking the average obtained is 0.20 ppm which is less than the tolerance limit. For red gram dhal, the average BHC residue is 0.42 ppm as purchased which was reduced only to 0.406 after cooking, thus indicating that for all the red gram dhal samples, BHC residue was almost double the tolerance level.

4. Malathion residue:

None of the pulse samples analysed had any detectable malathion residue before or after cooking. Since malathion

is widely used pesticide for cereal grain this information is of importance because it may either be due to the fact that malathion has not been used in the cultivation of the pulses analysed or the usage of malathion as a pesticide is well within specification for pulses that it does not leave any residue in the market sample. This needs further investigation.

In a study by Moorthy and Srivatsava (1978) with green gram dhal calculated dosage application of malathion and washing rubbing and cooking green gram dhal indicated that even at a dosage of 50 ppm the residual effect was only 3 ppm a level below the tolerance limit of 4 ppm. In the present investigation, since no malathion residue was observed either in straight market sample or after cooking homes one to think that application of malathion is well within the safe limit as far as the pulses studied are concerned and hence no detectable residue was present at the consumer consumption level.

5. Percentage decrease of pesticide residue in pulses due to cooking:

The percentage decrease in the pesticide residue of pulses after cooking was noticed and the results are tabulated in Table IX.

TABLE IX
PERCENTAGE DECREASE OF PESTICIDE RESIDUE IN PULSES
DUE TO COOKING

Pesticide Residue of	Greengram dhal	Blackgram dhal	Bengalgram dhal	Redgram dhal
DDT	ND	18.42	38.5	27.58
DDE	100	36.46	ND	44.44
BHC	24.27	11.92	25.92	3.33
Malathian	ND	ND	ND	ND

None of the pulse samples contained malathion residue. The DDT residue loss during cooking ranged from 18.42 per cent to 38.5 per cent. DDE residue was completely nil in the sampled green gram dhal and red gram dhal showed the highest residue level of 44.44 per cent of the BHC residue ranged from 3 per cent to 25 per cent. Higher the percentage loss, lower is the harmful and hazardous effects.

From the foregoing discussions, it is evident that barring a few samples of cereals and pulses, organochlorine and organophosphorus pesticide residue is not rampant in the

market samples of cereals and pulses studied. In general residues of DDT or DDE and BHC when present in isolated market samples is far above the tolerance level, thus, causing concern from the health point of view. Information on pesticide residue in market samples of commonly consumed foods specially cereals and pulses which form the staple food of masses of people needs concern from public health point. It must be enforced that from ^{time} to time, market samples are withdrawn and analysed for these residues in public health behaviours along with checking for adulteration and strict action taken at governmental level to check sale of undesirable samples in order to save the interest of the consumer.

Summary and Conclusion

V SUMMARY AND CONCLUSION

The main objective of this investigation was to study the common pesticide residues present in selected cereals and pulses as purchased from the market and after cooking. Accordingly three samples each of four cereals namely rice, wheat, sorghum and ragi and four pulses namely green gram dhal, black gram dhal, bengal gram dhal and red gram dhal were collected and analysed for Dichloro Dimethyl trichloro ethane (DDT), Dichloro Dimethyl ethane (DDE), Benzene hexachloride (BHC) and malathion residues both as purchased and after cooking. Analysis gave the following results:

1. The main DDT level in rice, wheat, sorghum and ragi were 0.0645 ppm, 0.022ppm, 0.02ppm and 0.153 ppm, respectively for the market samples which was reduced to 0.0395 ppm, 0.007 ppm, 0.008 ppm, and 0.095 ppm, respectively for the four cereals when cooked. All these values were well within the tolerance limit of 0.78 ppm.
2. DDE residue was not detectable in the rice sample. A value of 0.08 ppm, which was reduced to 0.03ppm, on cooking was observed for samples of one market source for wheat and a mean value of 1.5ppm

which was reduced to 1.35 ppm, on cooking was observed for sorghum samples and a mean value of 0.251 ppm, as purchased which was reduced to 0.0015 ppm was obtained for g ragi samples. Except for the single source sample of sorghum, all other had a value of DDE residue within the safe level of 0.78 ppm.

3. The BHC residue in cereals on an average were 0.026 ppm, for rice, 0.39 ppm, for wheat, 0.13 per sorghum, and 0.566 ppm for ragi. On cooking, the BHC residue value for rice was reduced to 0.01 ppm, for wheat to 0.17 ppm, for sorghum 0.16 ppm and for ragi 0.161 ppm. The BHC residue observed for wheat and ragi as purchased were above the tolerance level 0.25 ppm, which was however reduced below the tolerance level after cooking.
4. Wheat sample did not have any detectable amount of any malathion residue only one sample of rice had a malathion residue of 0.002 ppm which was reduced to nil after cooking. On an average, the malathion residue in sorghum was 0.018 ppm before cooking and 0.012 ppm after cooking. In

ragi only one sample had a malathion residue of 0.03 ppm before cooking which was reduced to zero after cooking.

5. DDT residue was not detected in green gram dhal samples, blackgram dhal had a residue of 0.038 ppm, which decreased to 0.037 ppm after cooking, in Bengal gram dhal DDT residue value was 0.745 ppm before cooking and 0.458 ppm after cooking, and 0.725 ppm before cooking which was reduced to 0.525 ppm after cooking in red gram dhal. DDT residue of one sample of Bengal gram dhal was above the tolerance limit of 0.78 ppm both before and after cooking whereas in red gram dhal only one sample had a value above the tolerance level which was reduced below the tolerance level on cooking.

6. The DDE residue values ranged from 0.003 ppm in one market sample of black gram dhal to 0.09 ppm in one market sample of red gram dhal. In most of the samples, it was not detectable and on cooking, it was reduced to a range of 0.001 ppm to 0.05 ppm.

7. BHC residue levels were found in almost all the samples. The mean value for green gram dhal was 1.3 ppm before cooking and was reduced to 0.78 ppm after cooking; for black gram dhal the main market sample was 0.13 ppm which was reduced to 0.1145 ppm after cooking. For Bengal gram, the market value of 0.27 ppm which was reduced to 0.02 ppm after cooking, and for red gram dhal, the market value was 0.42 ppm which was reduced to 0.406 ppm, on cooking. Both for Bengal gram and red gram dhal the values above the tolerance level of 0.25 ppm and in the case of red gram dhal even after cooking the value was almost twice as much as the tolerance level.
8. None of the pulses had any malathion residue both in the market sample and after cooking.
9. None of the cereals or pulses had any residue of carbamates.
10. The percentage decrease in the pesticide residue ranged from 32 to 100 per cent for cereals and 3.3 to 100 per cent for pulses in general.

The foregoing results indicate that the pesticide residue found in the staples like cereals and pulses as studied in this investigation is not alarming. Only a few samples of millets like sorghum and ragi had a high amount of DDT residue, and one sample each of blackgram dhal and red gram dhal had a high amount of DDT residue above the tolerance level which came down below the tolerance level after cooking. Of concern, is the BHC residue in red gram dhal, one of the most commonly used pulses which did not come down below the tolerance level even after cooking. Barring the above few samples, all others were well within the tolerance limit and the residue of the most commonly used pesticide malathion was conspicuously absent.

It is however, recommended that since not much information is available in such analysis of staple foods it would be of great practical relevance in the context of the present day slant in agricultural production and food augmentation to undertake more investigations along the following lines.

1. Periodic sampling of cereal grains from different markets and then their analysis for pesticides residues.

2. Animal studies on long-term consumption of pesticides at varying levels of intake.
3. Controlled experiments on application of pesticides to cereal grains and study of time lag and application concentration relationship to residue.
4. Studies on the effect washing, scrubbing and different methods of household processing and cooking in pesticides residue in cereal grains.
5. All the above aspects can be repeated on the other commonly consumed food items also.

The present investigation is only a limited study aroused of out of the investigator's interest in this problem of harmful effect of pesticide residues in foods and it is hoped that this would pave way to many investigations as mentioned above in different parts of the country. It is also recommended that state and central Governments in collaboration with regional food laboratories should view this consumer problem as an urgent public health problem requiring a multi-sectoral approach and would take steps to analyse from time to time

market samples of commonly consumed foods for consumer safety. Enforcement of laws towards this end and assurance of safe food to the consumers will go to a long way to assure good health and longevity to our masses.

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Appendices

APPENDIX I
PURIFICATION OF CHEMICALS FOR USE IN THE PESTICIDE
RESIDUE ANALYSIS

(i) Acetone:

It was purified from impurities by following the method of Branley (1916) commercial grade acetone was treated with potassium permanganate solution and allowed to stand for 3 to 4 hours more permanganate solution being added as the colour disappeared. After being distilled, the product was dried over calcium chloride and stored in brown bottles.

(ii) Hexane:

Morgan and Lowry (1930) method was used for purification. Commercial grade hexane was treated with concentrated sulphuric acid and shaken several times. It was next washed with 0.1 N solution of potassium permanganate in 10 per cent sulphuric acid and finally with 0.1 N solution of potassium permanganate in 10 per cent sodium hydroxide. The hexane was then washed with water, dried over metallic sodium, distilled and the fraction boiling between 65-70°C was used for analysis.

(iii) Chloroform:

To remove the traces of ethanol which may be present in chloroform, the method of Williams and Daniels (1924) was followed. Commercial grade solvent was washed with dilute sodium hydroxide solution and then with water, dried over fused calcium chloride and then over phosphorus pentoxide. It was fractionally distilled.

(iv) Benzene:

The procedure of Leonard et al., (1948) was followed. Commercial benzene was shaken successfully with concentrated sulphuric acid until free from thiophene then with water, dilute sodium hydroxide solution and water. It was dried by distilling over phosphorous pentoxide.

(v) Acetonitrile:

The procedure of Timmermans and Hennault Ronald (1930) was followed. The BDH grade sample was treated with sodium sulphate and phosphorous pentoxide distilled and used petroleum ether (40-60°C BDH) grade was redistilled before use.

Chromogenic Reagents:

(i) Ortho-Tolidine:

1.0g of ortho tolidine (Fluka buchs, Switzerland) dissolved in 100ml acetone was used as a chromogenic spray to locate lindane spots on their layer chromatographic plates with bluish green to prussian blue spots when exposed to sunlight or uv light.

(ii) Brilliant green:

0.5 g. of brilliant green (supplied by Scientific and Industrial Corporation India) was dissolved in 100ml acetone was used as chromogenic spray on the plate. On exposure to

bronine vapours wherever organo phosphate insecticides was present, orange coloured spot appeared (K.Visweswarish Raju et al., 1983).

Florisil and silicagel G were the other chemicals used.

APPENDIX II

EXTRACTION AND CLEAN UP PROCEDURE OF THE SAMPLES

One hundred grams of the sample was taken and blended for 5 minutes with 200 ml acetonitrile, filtered and repeated the blending with another 200 ml of acetonitrile and filtered. The acetonitrile was transferred to the separating funnel. 100 ml and was hexane, shaken well, decanted the hexane layer. Repeated the extractions there three times with 100ml hexane. Combined all the hexane extracts were collected acid and about 15 g of anhydrous sodium sulphide added and the concentrated the hexane to 5 ml in the rotary evaporator (Mendes , 1971).

Column Chromatography:

Packed the column (20 mm ind) with activated flouride (10 cm) topped with 1 cm anhydrous sodium sulphate, prewetted the column with 40-50 ml petroleum ether. Transferred to hexane extract to the column allowed it to pass through at a rate of 5 ml minute. Rinsed the flask twice with about 5 ml portions of petroleum ether. Poured rinsings on to the column. Rinsed the walls of the tube with additional small portions of petroleum ether and eluted with 200 ml of 6 per cent ethyl ether in hexane

at 5ml/minute. Change the receiver and eluted with 200 ml of 50 per cent ethyl ether in hexane. Concentrated the each eluent to suitable known volume in a rotary vacuum evaporation.

Tested 6 per cent of eluent for chlorinated pesticide such as aldrin, EHC, DDE, DDD, O-P-DDT, p-p-DDT, hepta chlor epoxide, lindane methoxychlor, mirex and perthane, poly - chlorinated biphenyl and phosphate pesticides. Second eluent was tested for chlorinated pesticides like dieldrin, and endrin and phosphate pesticides, diazinon and methyl parathion. Third eluent was tested for malathion.

The detection and estimation was done by thin layer chromatography and gas liquid, chromatography.

APPENDIX III
DETECTION OF PESTICIDE RESIDUE

(i) Preparation of the plates:

40 g. of silica gel was made into slurry with 90ml of distilled water and transferred to an application. The slurry was spread uniformly on the glass plates (20 x 10 cm.). After the silica gel was set on the glass plate for half an hour, it was activated at 110°C for 2 hours. After activation, the plates were cooled to room temperature and stored in a desiccator until subsequent use as solvent.

(ii) Spotting:

Grades concentrations of each under test (0.5, 1, 2, 5, 10 mg) were spotted on the thin layer chromatographic plate using a lamb dipipette or standard nanolitre micro capillaries.

(iii) Detection and Identification of Spots:

The test sample solution was spotted with the help of lambda pipettes 15mm from the lower edge of thin layer chromatographic plate and the solvent was run upto 15-18 cm by keeping it in the developing chamber. The plates were removed they were dried and sprayed with chromogenic reagent. The various components were detected and identified by running the standard samples and comparing the R_f values.

APPENDIX IV
QUANTIFICATION OF THE RESIDUE

Gas Liquid Chromatography

A varian rocrograph series 1400 equipped with a 6 ft x 1/8 in i.d. stainless steel column packed with 5 per cent G C_g in chromosorb. of 60-80 mesh was used. Nitrogen (50ml/min) was used as a carrier gas. Electron capture detector with tritium foil was employed. The injector column and detector were operated at 210°C, 190°C and 200°C respectively at 8×10^{-10} range. Aliquots of hexane extracted insecticide (clean up extract) from water were injected to GLC and the different insecticide peak were identified and quantified with respect to standards.

APPENDIX V

Details on Pesticide Residue Values for Individual SamplesDDT RESIDUES IN CEREALS BEFORE AND AFTER
COOKING

Market source	DLT	Rice		Wheat		Sorghum		Ragi	
		BC	AC	BC	AC	BC	AC	BC	AC
1	1	0.17	0.053	0.005	0.001	ND*	ND	0.09	0.08
	11	0.10	0.12	0.012	0.002	ND	ND	0.82	0.62
	111	0.09	0.043	0.001	0.003	ND	ND	0.35	0.11
2	1	0.037	0.004	0.02	0.01	ND	ND	0.05	0.031
	11	0.051	0.017	0.03	0.019	ND	ND	0.008	0.001
	111	0.03	0	0.009	0.009	ND	ND	0.012	0.009
3	1	ND	0.060	0.009	0.008	0.04	0.002	0.009	0.005
	11	ND	0.009	0.012	0.007	0.009	0.017	0.018	0.001
	111	ND	0.020	0.069	0.006	0.018	0.009	0.072	0.002

DDE Residues in Cereals Before and After Cooking

Market source	DDE	Rice		Wheat		Sorghum		Ragi	
		BC	AC	BC	AC	BC	AC	BC	AC
1	1	ND	ND	0.19	0.08	2.9	1.79	ND	ND
	11	ND	ND	0.02	0.01	3.2	2.82	ND	ND
	111	ND	ND	0.03	0	2.8	2.7	ND	ND
2	1	ND	ND	ND	ND	ND	ND	ND	ND
	11	ND	ND	ND	ND	ND	ND	ND	ND
	111	ND	ND	ND	ND	ND	ND	0.0012	0
3	1	ND	ND	ND	ND	0.099	0.005	0.080	0.002
	11	ND	ND	ND	ND	0.011	0.001	0.010	0
	111	ND	ND	ND	ND	ND	ND	0.010	0.001

*Not Detectable

DDT RESIDUE IN PULSES BEFORE AND AFTER COOKING

Market source DDT		Green gram dhal		Black gram dhal		Bengal gram dhal		Red gram dhal	
		BC	AC	BC	AC	BC	AC	BC	AC
		1	1	ND	ND	0.0069	0.005	1.92	0.93
	11	ND	ND	0.0071	0.006	0.09	0.07	ND	ND
	111	ND	ND	0.0072	0.0071	0.99	0.82	ND	ND
2	1	ND	ND	0.009	0.003	ND	ND	0.53	0.21
	11	ND	ND	0.012	0.011	ND	ND	0.72	0.62
	111	ND	ND	0.0088	0.008	ND	ND	0.73	0.46
3	1	ND	ND	0.19	0.082	ND	ND	0.83	0.68
	11	ND	ND	0.01	0	0.490	0.017	ND	ND
	111	ND	ND	ND	ND	ND	ND	0.75	0.56

DDE Residue in Pulses before and after cooking

Market Source DDE		Green gram dhal		Black gram dhal		Bengal Gram dhal		Red gram dhal	
		BC	AC	BC	AC	BC	AC	BC	AC
		1	1	ND	ND	ND	ND	ND	ND
	11	ND	ND	ND	ND	ND	ND	0.09	0.05
	111	ND	ND	ND	ND	ND	ND	0.06	0.02
2	1	ND	ND	ND	ND	ND	ND	ND	ND
	11	ND	ND	ND	ND	ND	ND	ND	ND
	111	ND	ND	ND	ND	ND	ND	ND	ND
3	1	0.08	0	ND	ND	ND	ND	ND	ND
	11	0.02	0	ND	ND	ND	ND	ND	ND
	111	0.02	0	ND	ND	ND	ND	ND	ND

BHC RESIDUE IN PULSES BEFORE AND AFTER COOKING

Market Source	BHC	Green gram dhal		Blackgram dhal		Bengalgram dhal		Redgram dhal	
		BC	AC	BC	AC	BC	AC	BC	AC
1	1	2.26	1.72	0.07	0.069	0.05	0.019	0.049	0.039
	11	ND	ND	0.01	0.01	ND	ND	0.061	0.059
	111	ND	ND	0.10	0.09	0.01	0.001	0.039	0.038
2	1	0.20	0.17	0.30	0.27	0.97	0.72	0.83	0.80
	11	0.18	0.06	0.09	0.08	0.082	0.74	ND	ND
	111	0.13	0.04	ND	ND	0.37	0.13	0.79	0.73
3	1	0.91	0.62	ND	ND	0.03	0.029	ND	ND
	11	0.89	0.82	ND	ND	ND	ND	0.40	0.38
	111	0.32	0.01	ND	ND	0.11	0.09	ND	ND