CHAPTER-I

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“There is no alphabet without the power of creating magic, there is no plant root which does not have medicinal value; there is nothing totally useless; what is rare is the person capable of putting a thing to its proper use” --- Rigveda.

The term “Environment” can be defined as the sum of all social, economical, biological, physical or chemical factors which constitute the surroundings of man who is the creator and moulder of his environment. All human induced activities, big or small cause an impact on the environment. During the last few decades the global environment has gone through serious challenges and changes. There is deep anxiety about the increase of pollutants in the atmosphere and accumulation of toxic chemicals in soil and water bodies. Our immediate concern is the quality of space we live in, the purity of air we breathe, the food we eat, the water we drink and the resources we draw from our environment to support our economy.

Rapid industrialization, population explosion, urbanization and indiscriminate use of pesticides in agriculture have created problems of environmental pollution attaining severe dimensions day by day all over the world in general and developing countries in particular. Environmental pollution has led to the deterioration of the quality of air, water and land. The deleterious effects of pollutants on human, animal, plant life and even on our climate have been well
recognized. Now the threat to human beings comes mainly from the destruction of the earth’s environment. This realization has brought together the heads of 150 nations for a historic “Earth Summit” at Rio-de-Janeiro (Brazil) in 1992 that generated new global awareness. India is in the foremost of the industrially developing countries with a high rate of industrial development. Industries such as chemical, pharmaceutical, electroplating, textile, pulp and paper and Agri-based are among the most important for growth and maintenance of modern society. Awareness has also been growing that certain food contaminants (pesticide residues) may pose risk to human life and to the quality of the environment.

1. Importance of Pulse crops

India is the major country in the world that grows a wide variety of pulse crops. They are grown in an area about 22,000,000 hectares producing about 9,800,000 tons of grain pulses that accounts for 18% of the total cropped area under food grains in India. Andhra Pradesh occupies 7th place in pulse crop production. Black gram and green gram are the two important pulse crops of Andhra Pradesh. These are fast growing warm season dry land crops. Black gram (Vigna mungo) is one of the most highly prized pulses in India. It is rich in phosphoric acid, 5-10 times more than other pulses. Green gram (Vigna radiata) is also an important pulse crop and unlike other pulses, the seeds are easily digestible and free from heaviness or flatulence. But the farmers could not harvest expected yields due to
the attack of uncontrollable pests. To overcome the hurdle and produce maximum yield, the farmers are repeatedly spraying various kinds of pesticides and plant protection chemicals.

2. Pesticide use in India

Use of pesticides in India began in 1948 when DDT was imported for malaria control and BHC for locust control. India started pesticide production with manufacturing plant for DDT, BHC and HCH in the year 1952. In 1958 India produced over 5,000 metric tons of pesticides and at present India produces about 1, 39,000 metric tons of pesticides of 125 technical grades and over 800 formulation units.

The economy of India, like many other developing countries, depends heavily on agriculture and agri-based industries. The green revolution in India has been possible only because of the impetus given to agriculture through the energy sector, fertilizers, pesticides and by the effective land and water resource management.

The term pesticide covers a wide range of compounds including insecticides, fungicides, herbicides, rodenticides, molluscicides, nematocides and plant growth regulators. Their extensive use has led to environmental problems. Of the total annual consumption of pesticides, 50% is used for cotton alone, 17-18% for rice and 6-7% for millets, pulses and oil seeds. Approximately 80,000 tons of technical grade pesticides are applied each year on the crops.

Use of pesticides on vegetables, fruits and plantation crops is also more intensive nowadays. Andhra Pradesh stands first place in
the highest use of pesticides (20%) followed by Punjab (10%), Tamilnadu (9%), Karnataka and Gujarat (6%). Among pesticides, the insecticides are used to the highest extent (about 72%), followed by fungicides (14%), and herbicides (11%) in India. Particularly in Costal Andhra Pradesh where the pulse crops are grown round the year organophosphorus (OP) pesticides are used very frequently to control stem borers and fruit borers that destroy the crop affecting loss up to 20-30%.

Costal Andhra region is famous for black gram and green gram cultivation as second crop after paddy. In Telangana and Rayalaseema regions both in kharif and Rabi seasons these pulses are grown as rain-fed crop. Generally the pests attack these crops at the time of flowering and fruiting stage. Farmers repeatedly apply insecticides namely chloropyriphos 20% EC, Diclorophos and Quinalphos to control pests. The farmers prefer chloropyriphos because of its broad spectrum nature.

Pesticides application on crop lands appears to be imminent to protect crops and secure good yield. But, over use and/or abuse of pesticides causes environmental pollution harmful to entire life on the planet. Since pesticides are used on crops in the form of foliar spray, due to run-off the excess amount of pesticide reaches to the soil and binds with soil particles. Through this process the chemical pesticides are entering into the ecosystem and living systems.
3. **Insecticides**

Insecticides are the compounds which are effective against insects. Many insecticides have been developed and used to control various species of insects. The insecticides are mostly applied as sprays, but a few are applied as dusts, aerosols, fumigants and baits. The majority of insecticides are synthetic organic chemicals and nerve poisons. They act by inhibiting the organisms or interacting with other target sites vital to the proper functioning of the insect’s nervous system. Some insecticides act by blocking essential processes such as respiration. Although, there are many synthetic organic insecticides, (1) Chlorinated hydro carbons or organo chlorine compounds, (2) Organo phosphorus compounds or organo phosphate compounds and (3) Carbamates are the three major categories.

### 3.1 Chlorinated hydro carbons or organo chlorine compounds (OCC)

These are called organochlorines and first developed commercial organic insecticides ex. DDT, Aldrin, Chlordane, Dialdrin, Endrin, Lindane and Heptachlor.

### 3.2 Organo phosphorus compounds or organophosphate compounds (OPC)

These are the most toxic among the insecticides and are dangerous not only to insects but also to mammals. Many of these
compounds are in the “super toxic” category of human poison. ex. Chloropyriphos, Malathion, Parathion, Diarzinon, Guthion and Phenothoate.

3. 3 Carbamates

These are derivatives of carbamic acid (HO-CO-NH₂) and are widely used for worm control on vegetables ex. Aldicarb, Carbofuron, Sevin, Zectran, Bygon, Temik and Pyrethrins.

Organochlorine (OC) insecticides were banned or restricted after 1960 in majority of the technologically advanced countries. The introduction of organophosphate (OP) insecticides began in the 1960s, carbamates in 1970s and pyrithroids in 1980s. The introduction of herbicides and fungicides during 1970-1980 played significant role in pest control and agricultural output.

4. Organophosphate (OP) Insecticides

Since the restriction or ban on the use of organochlorine insecticides, organophosphate insecticides became the most widely used insecticides today. More than 40 of them are currently registered for use and all of them have the risk of acute and sub acute toxicity. All apparently share a common mechanism of cholinesterase inhibition and can cause similar symptoms. Exposure to the same organophosphate by multiple routes or to multiple organophosphates by multiple routes can lead to serious additive life toxicity. Hence, it is important to understand wide range of toxicity of these agents and variation in continuous absorption.
5. Toxicity of organophosphate insecticides

These are very toxic to insects and mammals primarily due to phosphorylation of the acetyl cholinesterase enzyme (AChE) at nerve endings. As a result, there is a loss of available AChE and in turn the effected organ becomes over stimulated by the excess acetylcholine (ACh, the impulse-transmitting substance) in the nerve ending. The enzyme is critical to normal control of nerve impulse transmission from nerve fibers to skeletal muscle cells, glandular cells, autonomic ganglia and central nervous systems (CNS). The symptoms of poisoning manifest when some critical portion of the tissue enzyme mass was inactivated by phosphorylation.

Depending on dose, the loss of enzyme function allows accumulation of ACh peripherally at cholinergic new effector junctions and autonomic ganglia (nicotinic effects), as well as central nerves. At cholinergic nerve junction with smooth muscle and gland cells, high ACh concentration causes muscles contraction and secretion respectively. At skeletal muscle junctions, excess ACh may not only cause muscle twitching, but also weaken or paralyze the cell by de-polarizing the end plate. In the central nervous system high ACh concentrations cause, in-coordination, depressed motor function and respiratory depression. Organophosphate poisoning leads to death by increased pulmonary secretions coupled with respiratory failure. Recovery depends ultimately on generation of new enzyme in all critical tissues.
Organophosphates are efficiently absorbed by inhalation, ingestion and skin penetration. There is a considerable variation in the relative absorption by these various routes. For instance, the oral LD$_{50}$ of parathion in rats is between 3-8 mg/kg, which is quite toxic and is equivalent to dermal absorption with an LD$_{50}$ of 8 mg/kg. On the other hand, the toxicity of phasoline is much less by the dermal route than the oral route, with LD$_{50}$ of 1500 mg/kg for oral route and 120 mg/kg for dermal route respectively. In general, highly toxic agents are more likely to have high-order dermal toxicity.

6. History of Chloropyriphos

It is an organophosphate insecticide first developed by I.G. Farben of Germany in 1930. Chloropyriphos is a broad-spectrum organophosphate insecticide. It has been registered in Australia for crop protection and pest control. It has been manufactured by Dow elanco, formally the Dow Company in U.S. since 1965. The common brand names are Dursban (for domestic use) and Larsban (for Agricultural use) produced under trade names of Bordan, Detmot-UA, Dowco-179, Dursban, Empire, Eradex, Larstan, Paquant, piridane and Stepind.

Chloropyriphos is used for the control of Coleopteran, Diptera, Homoptera and Leptoptera insects present in soil and sprays on foliage of a wide range of crops namely nuts, vines, vegetables (potatoes, asparagus), grains (rice, cereals, maize, sorghum), cotton,
pulses, mushrooms and ornamentals. It is also used in the control of termites, fleas and cockroaches. The flea shampoos and sprays of pet-animals are prepared with chloropyriphos.

7. Ecological effects of chloropyriphos

7. a. Persistence and bio-accumulation

Chloropyriphos is moderately persistent in soil. The half life usually lies between 11 and 180 days but can range from two weeks to one year, depending on soil type, climate and other conditions. In water, at pH 7.0 and at 25°C temperature the half life was 35-78 days. Residues persist in plants from 10 to 14 days and research studies indicate that chloropyriphos may accumulate in some crops. Chloropyriphos has the tendency of bio-accumulation. It has been found to accumulate in the fat tissue of rats, wing fat tissue of northern bobwhites and in the tissue of fulvous whistled ducks of Florida. Research studies conducted in fish revealed that the bio-concentration values range from 58 to 5100 days.

7. b. Eco-toxicology

Chloropyriphos is highly toxic to fish and aquatic invertebrates of both estuarine and marine ecosystem. It binds tightly to soil particles and is relatively insoluble in water. It persists in the sediments of aquatic habitats and is hazardous to benthic invertebrates and other bottom feeders. The domestic use of Dursban, led to the death of 500 Bream in Georgia pond into which a swimming pool water backwashed. The chloropyriphos that was used in the pine
seedling treatment resulted in killing of fish in a saline river watershed in Arkansas. The chloropyriphos (Dursban) used for termite eradication, contaminated a lake water through an underground water supply and killed 2000 bluegills. It is highly toxic to honey bees and is hazardous to other pollinating bees and birds.

7. c. Effects on Plants

Although chloropyriphos is expected to be non-toxic to plants, it has been observed to be toxic to a number of plants. Emergence of carrot and onion seedlings was delayed and size reduction was noticed by chloropyriphos treatment. Treatment of grapes with chloropyriphos during bud breaks led to fruit damage known as ridging. It is also reported that it induced abnormalities in cell division and chlorophyll deficiencies in barley.

7. d. Effects on soil organisms

Earthworms are sensitive to chloropyriphos poisoning, although the toxic dose vary among different species. Lumbricus rubellus, a commercially available species, is about ten times more sensitive than Eisenia fetida another commercial species. Chloropyriphos affects the growth of many soil fungi, nitrogen fixing bacteria and blue-green algae. The negative effects of chloropyriphos exert profound influence on the nitrogen economy of agricultural soils.
7. **e. Effects on Domestic Animals**

The domestic animals like cats, newborn calves, adult bulls and new born pigs are most sensitive to chloropyriphos exposure. Cats have been poisoned or killed following of their owner’s home treated with chloropyriphos. It is also reported to cause delayed neuropathy in cats.

New born calves are about 30 times more sensitive to chloropyriphos than older calves. Bulls have been killed by their exposure to this chemical. Lower doses induce a decline in sperm production. Chloropyriphos-containing aerosol spray resulted in the death of pigs, when it was used to treat wounds resulted during the removal of umbilical cord and the tail.

7. **f. Ecosystem-level Effects**

Chloropyriphos affect entire ecosystem where the mortality of a sensitive species has a direct effect on the other species. These kinds of interactions have most often been studied in a number of aquatic ecosystems. As early in 1968, biologists noticed such kind of effects of chloropyriphos, when it was first used to control mosquitoes. Application of Dursban to eight experimental ponds in California resulted in reduction of predaceous herbivorous insects and as a consequence herbivorous crustaceans and rotifers increased. Sequel to this phytoplankton (Blue green algae and Diatoms) increased dramatically, that formed into algal blooms. The livestock and wild life was affected by drinking water infestation with algal
blooms. The researchers also pointed out that, Dursban created an ecological imbalance that was apparently favorable to the insects.

Research studies made during 1986 and 1987 in Minnesota, reported an increase in algal abundance and decrease in invertebrate species, insect abundance and fish growth (Fathead minnows) when chloropyriphos (0.5 ppb concentration) was used. Ecosystem-level effects have also been measured in terrestrial ecosystems. A four year study of effects of chloropyriphos on plant communities revealed that it changed the complete balance among plant species on the disturbed soil and increased broad leaved plants. The researchers noticed that by the use of this chemical for elimination of insects has profound influence on the establishment and subsequent development of natural plant communities.

8. Pesticide Residues in Food

The world food summit of November 1996 focussed attention on matters relating to food security and had a critical look at high input agriculture, particularly chemical use that results in serious health and environmental hazards. Food security is a complex issue governed by socio-economic and political factors. Population explosion is one of the major issues of the developing Asian countries. The population of Asia has doubled from 1.2 billion to 2.6 billion between 1950 and 1985 and today it touched 6.5 billion out of the world total of 10.6 billion. It is projected to climb to 7.3 billion by 2012, in Asia.
In India the problem of pesticide residues present in cereals, pulses, fruits, vegetables, milk and milk products is a serious issue. The over use, abuse or misuse of pesticides can have serious consequences on food. Large scale use of pesticides contaminates food and poses health risks even in small quantities. DDT in human breast milk and endocrine-disrupting pesticide residues are the best examples to quote. Certain classes of pesticides like organophosphates have a common mode of action and their effect may be cumulative. The prevalence of pesticide contaminated toxic products in many developing countries is of high concern for consumer safety in these countries.

Internationally, many countries have restricted the use of these toxic products by establishing country specific legal directives to control their levels in food through maximum residue limits (MRLs). As a result, fruits and vegetables with acceptable residue levels in one country may be rejected in another, a situation that leads to serious problems in international trade. Moreover, a food exporting country may allow the use of pesticides that are not registered in the importing country, eventually leading to rejection of shipment by the importer. The health risk of pesticide residues in infants and children is to be viewed correctly.
9. Food pollution Episodes

In India the first report of poisoning due to pesticides was from Kerala in 1958, where over 100 people died after consuming wheat flour contaminated with parathion. In U.S. almost 2,000 people fell ill after eating watermelon contaminated with aldicrab in 1985. The Malva region of Punjab state (India) known for its rich agricultural produce and cotton farming through large scale use of pesticides is today battling environment-related health problems that include a noticeable rise in cancer incidence, kidney ailments and infertility. The high pesticide levels in the environment greatly affected the cattle too. Their milk yields have gone down and the cows did not conceive properly. The people are suffering from arthritis, health disorders that effect reproduction and responsible for the increase in the number of childless couples.

10. Chloropyriphos residues

Chloropyriphos residues have been found in food, water, soil and air. Between 1990 and 1992 U.S. Food and Drug Administration (FDA) found chloropyriphos in tomatoes, oranges, peaches, cherries, bananas, apples, grapes, orange juice, tea and several types of processed oriental foods including noodle soup. During 1992 and 1993 chloropyriphos residues were found in 16 of the 42 foods.

Chloropyriphos residues have also been found in meat and dairy products. For example, residues were found in mutton, beef
and pork, due to the use of chemical pesticide to keep these items free from flies, ticks and lice. The fat found to possess high chloropyriphos concentration than the other tissues. A survey conducted in America reported that 82% of Americans during 1994 have chloropyriphos residues in their urine. The tests conducted by a Delhi based NGO (Centre for Science and Environment) revealed the presence of chloropyriphos residues in Indian Coco-Cola and Pepsi-Cola.

During 1992-1994, 26 red-tailed hawks, one coopers hawk and one barn owl were killed in Central California due to agricultural spraying of chloropyriphos. Over 80 incidents of fish poisoning have been reported to the Ecological Incidents Information System between 1992 and 1999. The common fish species that were killed include darters, gar, bream, trout, bass, sunfish and catfish. Many incidents of death of American robins after chloropyriphos use on residential lawns have been reported from many areas of U.S.A.

11. The Maximum Residue Limits (MRLs)

It is the legal limit of pesticide allowed in food or animal feeds and it is expressed in mg/kg produce. The FAO and WHO have been evaluating the safety of residues in food since 1962 and establishing maximum residue limits (MRLs) to ensure that pesticides are not over used and that any residue is safe for human consumption. Indiscriminate use of pesticides leads to several adverse effects. The persistent nature of pesticides especially insecticides is a serious
problem as their residues present in all types of commodities, soil and physiological parts of human, animal and plants bodies.

Afore said information on pesticides and their negative effects prompted to choose the present line of research work to determine the possible phyto-toxic effects of chloropyriphos on the two locally important pulse crops and to quantify the pesticide residues and their persistence in these crop plants.

The results of proposed study and its conclusions would help to understand the environmental problems posed by chloropyriphos and to emphasize the need to assess the soils and agricultural commodities of pulse crops for their pesticide MRLs from Andhra Pradesh (India), since such studies were scanty and such assessment was not so far made by National Regulation Authority (NRA).