GENERAL
INTRODUCTION
Environment is the representative of physical components of the earth where in man is the important factor influencing it (Goudie, 1984). The environment of any living organism is never static, but changes, sometimes slowly and some times rapidly, which may benefit or harm man. With the increase in scientific knowledge, man is able to modify his environment, much more than any other organism, to suit his needs. His progress in the fields of science and technology would not have been possible, had he not expiated natural resources. There is no environment, which has not been approached by him. The consequence of all this is a global disaster. Man today equipped with a variety of skills and superior technology has ruined the natural resources.

Environmental pollution is one of the most horrible ecological crises to which all the living organisms are subjected today. It is due to urban-industrial technological revolutions and speedy exploitation of all natural resources. Rapid industrialization aggravated the problem of pollution more than any other cause and left with us polluted rivers, contaminated soil, depleted wild life and exhausted natural resources. Today the vary environment has become contaminated; undesirable and therefore harmful for the health of living organisms. Man has realized that any further effort to disturb the balance between abiotic and biotic world would lead to catastrophe.

Of the total environment that is distributed, aquatic system is one of the worst affected. Pollution of water bodies has increased steadily due to rapid population growth, industrial proliferation, urbanization and wide sphere of human activities. Many rivers of the world are receiving heavy flux of sewage,
industrial effluents, domestic and agricultural wastes, which are full of having highly toxic and hazardous chemicals. Million tons of toxicants like metallic wastes, phenols, aldehydes, ketones, amines, cyanides, plasticizers, toxic acids, corrosive alkalines, dyes, biocides, radioactive wastes, and thermal pollutants are entering every year into the aquatic environment (Ostrander and Malin, 1990). In addition, billion tons of oil per year is spilled through mining operations and other geophysical modifications. It has been reported that 180 million liters of toxic effluents are released into Periyar River every day by various industries in Greater Cochin area. It results in the participation of various chemical substances with natural cycles, there by BOD of this river has increased to 16.5 against the normal content of 5.0.

Pollution of natural water bodies has become a common phenomenon in developing countries (Wepener et al., 1992). Time is perhaps not too far to search for pure and clean water for drinking purpose. Water is considered as polluted when it is altered in physical, chemical and biological characteristics which may cause harmful effects on human and aquatic biota (Sharma and Kaur, 1994). It represents the state of deviation from the pure condition, there by its normal function and properties are affected. Water pollution obstructs the normal use of water for irrigation, industries, public water supply and aquatic life. Degradation of water quantity is today's burning problem of both developed and developing countries, including India (Dissanayake and Jayatilaka, 1980; Pande and Das, 1980)
Water is widely distributed on the earth in various forms. However, much of water is not put to proper use of the world precipitation. A 79% of the water is not useful to man, since it falls into the sea. In the remaining of 21% water that falls on land, 13.4% of water gets evaporated, only 7.6% of water is available as run off in streams and rivers and get into the ground. Nearly man can control 3.8% water, but in reality the water can be controlled by man, that is controlled is 3.5%. As a result the fresh water is under the control of man is only 0.3% (Rao et al., 1990). This meagre percentage of water is also subjected to pollution in many ways.

Water forms an essential part of all organisms. Its unique properties made it a basis for the existence of life on earth (Ranganatha Rao, 1986). Most of the biochemical reactions in living cells occur in aqueous environment. Water acts as a solvent for various molecules, helps in ionization of salts and is medium for the excretion of nitrogenous waste products, metabolites and products of detoxification (Ramakrishna et al., 1994).

Much of the ill health in India and other developing countries is largely due to lack of safe drinking water. More than 50% of illness in India can be cut down by providing safe drinking water.

1.1 WATER POLLUTION

Water pollution is one of the most important problems being faced by both developed and developing countries in the world today. Earth’s water resources are limited and erratic supply and pollution further restricts the availability of water for diverse human uses like drinking, cooking, cleaning,
reaction, aquaculture and industry. Most of the rivers in the world (more
prominently in India) are full of filth and stench of polluted waters. Although the
pollution of a particular water body can always be traced back to some source
like an industry or sewage or agricultural run-off, in general, water pollution is an
inevitable fall out of development (Subramanyam and Sambamurthy, 2000). The
following are the ways by which different toxicants enter water bodies.

i. Disease-causing organisms - Especially parasities, bacteria and viruses,
which often enter water with human sewage.

ii. Synthetic organic compounds in the form of industrial, household and
agricultural, chemical, as well as water-treatment chemicals added
deliberately and the products formed by the reaction of these with other
contaminants.

iii. Inorganic compounds and mineral fibers such as asbestos and heavy
metals, discharged directly into water by certain mining and industrial
operations and also entering water as fallout or in precipitation from the
atmosphere.

iv. Radioactive substances from commercial and military applications of
nuclear energy.

v. Oxygen-demanding wastes - namely, organic compounds contained in
sewage and some industrial effluents, whose biological or chemical
degradation depletes dissolved oxygen.
vi. Plant nutrients such as nitrogen and phosphorous from sewage and agricultural run-off.

vii. Sediments from erosion caused by agriculture (or) construction.

viii. Thermal discharges from power plants and certain industrial facilities.

Water pollutants also can be classified by their effects; direct impact on health in the form of bacterial (or) viral disease; production of cancer; genetic defects and birth defects; other varieties of acute and chronic toxicity to people and effects on ecosystems through which an impact on human beings may subsequently be felt.

**Water pollution in India**

Most of the water resources in India are chronically polluted due to industrial discharges including those of paper mills, textile, rayon, fertilizers, pesticides, detergents, synthetic drugs, antibiotics, oil refineries, photofilms, etc. The domestic wastes and industrial effluents being indiscriminately discharged into the nearby rivers, reservoirs, lakes and tanks with almost no pre-treatment, all the major Indian rivers such as Ganga, Yamuna, Tapti, Narmada, Sone, Chambal, Dana, Hoogly, Gomati, Damodar, Krishna, Cauvery, Brahmaputra, Tungabhadra, Godavari and others are severally polluted with industrial effluents and sewage discharges (Konhar et al., 1991). Ganges, the prestigious river, which flows from mighty Himalayas, has been heavily polluted near Kanpur due to the in flow of industrial wastes from tanneries and textile mills and also chemical, metal and surgical industries (Chakrabarthy et al., 1965); while the Gomati river
has been polluted with the wastes from distilleries and sugar factories (Khan, 1981). In Rhihand reservoir, which is on the river Ganges, the effluents of Kanoria chemicals, chiefly manufacturing caustic soda, make their entry into it. Mercury pollution has been noticed due to its use in the electrolysis of caustic soda. Panchet reservoir (Bihar) is polluted by the confluence of sindrinulla effluents from Sindri fertilizers. Dal and Nagin lakes in Kashmir are severely polluted by sewage (Konhar et al., 1991). The water of river Subernarekha which flows through the industrial belt of Bihar at Gnat Sita gets the effluents from Hindustan copper limited which caused heavy damage to the biota, especially to the life of fish in the river (Munshi and Singh, 1992) in Orissa. Water from the rivers Mahanadi and Katjori, as well as form the century old Taladanda canal, are quite futile for human consumption because of severe pollution. Orissa high court has recently directed the Government to act immediately, considering the reports of the Pollution Control Board to take necessary action to prevent pollution of these water bodies. Periyar in Kerala carries the effluents of five chemical industries. River Cooum flowing through Chennai has become so much polluted by domestic sewage that even plankton have not been able to thrive in it. It is estimated that one litre of Cooum river water contains as much as 900 mg of iron, 275 mg of lead and 32 mg of zinc. Almost all the rivers are polluted by several types of pollutants and their effects reflect upon the productivity of fauna. Some Indian rivers and their major sources of pollution are listed in Table 1 (Verma and Agarwal, 1986).
Most of the effluents released by the industries are reported to contain high amounts of chlorides and metals (Konhar et al., 1991). Marine water is also heavily polluted in India due to the release of various industrial effluents and oil slicks. Coastal water of Mumbai have been polluted to such an extent that the fish caught there are unsuitable for consumption. Oil slicks from ships along the oil route from the Gulf to South-East Asia, poor sewage disposal facilities in greater Mumbai and unchecked industrial pollutants have been polluting the coastal water of north Kolaba district (Statesman, Kolkata, May 15 1979). Recently heaps of dead fish were washed ashore between Kabolim and Vellao coasts in Goa due to dangerous effluent discharged from Zuari Agrochemical Fertilizer Factory. The tragic images of deadly oil spills threaten to set into motion an unprecedented ecological disaster. Ironically the oil that drives millions of vehicles around the world some times drives countless birds and animals to the most cruel death. However, the extent of pollution depends on the volume of the water body, the volume of effluents discharged and the characteristics of pollutants. Besides this the ecological processes is aided by the natural environment (Farrington and Westal, 1986).

**Water pollution in Andhra Pradesh**

An extensive study made in 28 villages of Prakasam, Nalgonda and Guntur districts in Andhra Pradesh proved that 600 among 21000 have been crippled ("bent block") for life by florosis. The effect has been mostly in children. In these areas a disease has been effecting the people leading to mottling and pitting of teeth, decay of bones causing deformation of the body
structure and classification of ligament tendon in addition to abdominal constipation, anemia and insomnia. It is attributed to high content of florine in the ground water.

Tungabhadra water near Kurnool became polluted by Paper Mill discharges (Manikya Reddy and Venkateswarlu, 1987). Similarly the Kovvur Caustic Soda Plant, the Rajahmundry Paper Mills on Godavari are cited as few examples of cause water pollution (The Hindu, September 1979). Environmental contamination by the effluents of a lead copper project (Hindustan Copper Ltd.) has resulted in a peculiar disease to cattle, paralysis of limbs followed in some cases by death in a village called Malapadu in Vinukonda taluk of Guntur district, Andhra Pradesh (The Hindu, September 1979). Reddy (1985) reported that in the twin cities of Hyderabad and Secunderabad, many women have suffered with abortions and children showed chromosomal damage due to pesticide residue in grapes. A rapid survey conducted by the Central Fisheries Extension Centre, Hyderabad revealed the mortality of large variety of fish during 1973 due to pesticides (Hingorani et al., 1973).

1.2 PESTICIDES IN INDIA

In India about 80,000 tons of pesticides are consumed/annum. About 40,000 tons of persistent pesticides are used in agriculture. The amount of pesticide consumption in India is very low, about 400 g/hectare as compared to anywhere else, but the persistent type of pesticides are being used, which have been banned elsewhere (Subrahmanyam and Sambamurthy, 2000).
The Insecticides Act of 1969, which came into force in 1971 regulates the import, manufacture, sale transport, distribution and use of these chemicals for the sake of prevention of risk to human beings and animals. The manufacture, import and use of chemicals (pesticides) can be initiated only after proper regulations, after a close scrutiny of the bioefficiency and safety of human beings, wildlife, birds, domestic animals, beneficial parasites, predators, pollinating insects etc., by the registration committee. Apart from recommending the registration for individual chemical, the committee also lays down the details of packing, labeling, approved usage, restrictions and precautions.

At present more than 122 pesticides are registered in the country. Endrin and parathion have been phased out and the use of dieldrin can be used in scheduled areas only, and that too on the advice of the Plant Protection Advisor to the Government of India for locust control.

**Pollution due to Pesticides**

With population explosion, there is heavy demand for the food production. Inspite of using powerful agricultural techniques along with the application of fertilizers and pesticides for good harvest, food is not sufficient for the increasing population. Hence man is now turning towards aquatic habitats to increase food production. Even fresh water bodies like ponds; lakes, pools etc. are now commercially exploited to get maximum fish production. Recently the Government of A.P also enacted a legislation providing auctioning of such water bodies for commercial utilization of fish production. If this is continued for long there is every possibility that fish reared in these ponds or pools may be
contaminated with pollutants from the nearby agricultural lands and thereby become un-fit for consumption.

There has been a considerable increase in agricultural production due to high yielding varieties of seeds, chemical fertilizers and insecticides. According to CRTR 50% of our food is lost due to pests and parasites. In order to control this loss, huge quantities of pesticides are used.

Pollutants are inhibitory environmental substances produced by the activity of the organism itself. All organisms generate environmental modifications, which arrest the organism’s growth. Man is not different and his pollution is exceptional only because of its volume, persistence and persiveness. Most organisms depend upon a large habitat volume or upon the mobility of themselves (or) their habitat to dissipate these toxic products. When the rate of pollutant production exceeds the rate of dissipation, accumulation of toxic levels may have adverse effects on animal metabolism.

The term pesticide includes a large variety of compounds of diverse chemical nature and biological activity, which are used to destroy (or) eliminate pests. Under the US Federal Environmental Pesticide Control Act, the term pesticide has been defined to include any substance or mixture of substances intended for preventing, destroying, repelling or mitigating any pest (Gupta and Satankhe, 1985).

A recent study of the World Health Organisation reveals that on an average, one person is poisoned every minute by pesticides in the developing
world (Radhakrishna Rao, 1984). Routes of pesticides entry into the environment are (a) surface run off and sediment transport from treated soils, (b) industrial wastes discharged into factory effluents, (c) direct application as aerial sprays (or) granules to control water inhabiting pests, (d) spray drift from normal agricultural operation, (e) atmospheric transport, (f) agricultural wastes and (g) accidental spills. Surface run off is generally considered to be the major mode of movement of pesticides and other chemicals into the aquatic environment (Edwards, 1973; Nicholson and Hill, 1970).

A number of pesticide factories are located near the aquatic ecosystems. Pesticidal factories located at Mathura, Faridabad and Agra release their waste products, which require 8000 times dilution to render them free from immediate harmful effects (Agarwal, 1983). The river Yamuna is quite often referred to as open sewer because of great degree of water pollution (Times of India, 1992). More than 50% of India’s economy is dependent upon agriculture and India’s agriculture has to go a long way to reach the yield of the advanced countries.

**Water pollution due to pesticides**

In recent years the use of pesticides to enhance agricultural productions has increased enormously, particularly in developing countries such as India. The pesticides can find their way with the run off water into water bodies and may adversely affect fish life. More and more pesticides are entering the aquatic system, hence in fisheries development, it is important to know the effect of pesticides on the reproductive potential of the fish (Birge et al., 1985). Reproduction in aquatic animals usually is the most critical function affected by
chronic stress. It is presumed that the study of chronic toxicity of insecticides on reproduction of fish will throw light on reproductive capabilities and ultimately on the survival potential of fish.

Pesticide contamination of water sources can result from the transport of only a small fraction of the pesticides applied at the soil surface. Pesticides are considered to be the major inputs not only in agricultural production but also in post-harvest operations particularly in storage.

Food pollution due to pesticides

The advancement in pesticides has helped to prevent crops from being destroyed and increase in agricultural but caused long lasting toxic effects on animals and human beings. Fumigants are widely used for harvesting cereals, pulses and nuts and for treating storage areas. They tend to disappear by volatilization and diffusion, when grain is processed and food is cooked. Applications of fumigants directly on animals to control insects add to their presence in meat, and so their use is not permitted on lactating animals.

The carbamate is partly broken down in plants to non-toxic compounds. Total diet studies indicate a daily intake of 0.02 mg of carboryl from meat, fish and poultry. Phenoxy herbicide and dithiocarbamate fungicides are found in very low level in food stuff. Food may serve as a vehicle for the transport and distribution of pesticides. A serious incident of poisoning by endrin, resulting in several deaths occurred in Saudi Arabian when bread prepared from wheat that was contaminated with this insecticide was consumed. In order to curb the 50%
loss of food material due to pests and parasites huge quantities of pesticides are being used (CFTRI, 1980).

Carbamates like aldicarb, have resulted in poisoning in consumers of treated food and they found in cucumbers, watermelons, squashes in the USA and Canada (Hall and Rumack, 1992) and in the Right Republic (Department of agriculture and Food, 1992). Oximes are harmful (Bismuth et al., 1992).

**Pesticide residues**

Pesticides have been used for a long time now and will continue to be used for decades to come, the major concern being the exposure of spray operators to the dangers of pesticides during mix-loading, spraying and disposal, cleaning of protective clothing and equipment and re-entry into sprayed zones.

Pesticide residues in agricultural commodities, food, livestock, poultry, feeds, soil and water have been a matter of great concern. Pesticides also enter human system through eggs, milk, through the feeding of contaminated fodder by the animals. Maximum residue limits for about 50 pesticides and their major metabolites have been laid down for important (not all) fruits, vegetables, food grains, meat, milk, eggs etc. Under Prevention of Food Adulteration Rules, more than 137 pesticides are registered under the Insecticides Act so far.

It is necessary for adopting uniform test procedures for assay of the pesticide residues as a prerequisite of their qualification in various products. In order to carry out the work of standardization of methods of test, Pesticides residue Analysis Sectional Committee (FAD 34) has been constituted.
More product standards will be formulated in the future on new items such as Botanic and Bio-pesticides. Recently Central Insecticide Act 1968 has registered neem based pesticides and bacterial based pesticides formulations namely Bacillus thorigenesis and Bacillus sphoricus. Latest analytical techniques are being introduced in the standards for affecting more accuracy in the test methods as pesticides are a high cost item today and also to ensure consumers protection.

There is extensive information on residues in fish from different parts of the globe. The highest quantity of DDT (1.3 gm/kg) has been recorded in fish and Atlantic croakers in the Estuary near Pensacola (Hansen and Wilson, 1970) which ultimately led to the banning of DDT by the Environmental Protection Agency (EPA) in the US (Anon, 1972). However the presences of other pesticides along with DDT in fish in alarming concentrations have been recorded from other parts of the world. Pesticides and organic pollutants in the top 100 to 150 gm layer of the sea in Narragonsett Bay in the US (Duce et al., 1972), high levels of OP residues in the water of Holland Marsh in southern Ontario. High levels of malathion (as high as 500 g/L) in the waters of Texas (Coppage et al., 1972) are some examples of environmental pollution. Residue levels of DDT up to 250 mg/kg and 235 mg/kg of DDE in eggs of Salmo gairdneri was reported Sodergren et al., (1978). These are only a few to mention.

Nature of pesticides

Pesticide formulations constitute technical grade material, diluents, stabilizers, surface active agents, for field applications directly. Pesticide
formulations such as dusting powder (DP), water soluble powder (WP), emulsifiable concentrates (EC), granules (G), soluble liquids (SC), solutions (Sol). The adjuvant material caused in the formulations should necessarily be compatible with the active ingredients, without adversely affecting in any way its biological activity or causing damage to the host or substrate or not be detrimental to the environment.

Emulsifiable concentrates (EC) are liquid formulations and blends of toxicants, solvents emulsifiers and stabilizers etc. The major requirements apart from active gradient content as specified in standard one, emulsifiable concentrates are emulsion stability, flash point test heat stability etc. These requirements indicate the performance characteristics of the materials and ensure compatibility with the solvent systems, suitable for formation of emulsion dilution with water monphyto toxicity.

The effectiveness of pesticides in pest control programmes largely depends on their quality, which includes the function of physical and chemical properties of the formulation.

Analysis of pesticides for standardization and quality control basically involves determination of the active ingredient (AI) content to know if the desired level of toxicants is present. The methods of estimation of AI of any pesticides are very specific and give acceptable results, which should be repeatable and reproducible.
Pesticides are used in large scale and often on long term basis have been found to result in toxic manifestation both in man and live stocks. As some of these compounds are very highly toxic, it is extremely essential to exercise great care in their usage. Pesticide poisoning may result from careless handling by the people engaged in its application processing and field or by accidents during the manufacture of the products.

**Biological uptake of Pesticides**

The potential exists for substantially increased pesticide exposures, if by choice of economic necessity; individuals begin to eat fish from more contaminated lakes (Peterson *et al.*, 1994). In fish, the principle mode of uptake of pesticides is through the gills (Holden, 1970), body surface and gastrointestinal system (Murphy, 1980), through integuement (Bowes, 1972) and by the ingestion of contaminated food (Macek *et al.*, 1969). However the portals of entry of the pesticides differ from organism to organism.

A particular insecticide may be very toxic to mosquitoes initially, and may not harm the birds at this applied concentration. But after repeated use, it might result in highly resistant mosquitoes. This also affects birds because of biomagnification of the insecticides in their food (Heckman, 1986).

**Hazards, risks and deaths in animals due to pesticides**

Hazard is defined as the ability of a pesticide to cause harm through skin, lungs and oral intake. Appraisal of hazard should take into account the onset of
poisoning symptoms, slow reversion to normality after the toxic effects have occurred (or) the lack of an effective antidote.

Rachel Garson's famous book "Silent Spring" gives a vivid description of the harm caused by misuse of pesticides. It has been reported that use of pesticides is responsible for the decline in population of white tailed eagles in Sweden, poisoning of Penguins and Seagulls in Antarctic, death of several thousand sea birds on the Irish coast and tigers in India. It is estimated that annually about 5,00,000 of accidents take place due to pesticides and 10,000 deaths occur (Employment News, 1992).

The use of a wide range of pesticides is important aspect of agricultural practice in both developed and developing countries. The knock down effect of pyrethroid compounds to insects coupled with their extremely low toxicity to warm blooded animals makes them suitable choices. But they are more toxic to fish (Mauck et al., 1976; Zitko et al., 1977; Mulla et al., 1978). The percentage of pesticides residue in the milk of mother in Guntur and Krishna districts is the second highest in the world (Rao, 1995).

Chemical pesticides are also known to contaminate food and water. The WHO has estimated that one million pesticide poisoning cases occur every year causing around 20,000 deaths per year globally (Parvinder Chawla, 1997). It is not surprising to note that an average Indian's body has the highest DDT levels in the world ranging to 12.8 to 31 ppm (Ravishankar and Thimmaiah, 1995). Pesticide poisoning may also lead to asthma, skin diseases, stomach disorders,
enlargement of liver psychological products and even to some extent degeneration of nerves often resulting in paralysis.

In fish, apart from their well-known cholinesterase inhibitory effect, organophosphates modify the activity of several other metabolic enzymes (Dalela et al., 1978; Mukhopadhyaya and Dehadri, 1980; Natarajan, 1981). The fish populations are components of food chain in aquatic ecosystem and any effect of such pollutants on fishes would naturally result in an imbalance in aquatic ecosystem. Many aquatic pollutants have been found toxic to fishes (Holden, 1972) and many investigations have been made to estimate the acute and chronic toxicity to such pollutants (Gupta et al., 1984; Kumar and Pant, 1984; Ghosh, 1987; Wang and Yew, 1987). Significant quantities of pesticides reach the rivers and the sea. These are mostly chlorinated hydrocarbons and mercuric salts. According to the World Health Organization the acceptable daily intake of DDT is 0.3 mg/person or 0.005 mg/kg body weight for man. DDT and other chlorinated hydrocarbons are non-biodegradable and their biological amplification concentration goes on increasing at successive tropic levels (Subrahmanyam and Sambamurthy, 2000).

DDT being lipophilic has the tendency to be absorbed by adipose tissues. Use of DDT has been banned in agriculture but people still use it for controlling Malaria. BHC is one pesticide which has 4 isomers-alpha, beta, gamma and delta. One of the components beta is (β) 10% in BHC. In the environment most of the pesticides degrade but beta isomer of BHC tends to accumulate and it is carcinogenic in nature. In BHC it is 10% but in butter oil, we can find 30% to
40%. The presence of DDT in population of Delhi is the highest when compared to any other place in the world. It is around 30 ppm (Subrahmanyan and Sambamurthy, 2000).

Elevated concentrations of chlorinated hydrocarbons endanger the survival of seabirds, mammals and fishes. The eggs of California pelican birds contained 115 mg/kg body weight of DDT. Polychlorinated biphenyls were found to be about 120 mg/kg. Due to this, the egg shells broke prematurely. Survival rates of eggs are reduced. In the sea fish high levels of DDT were reported (Subrahmanyan and Sambamurthy, 2000).

Reports of pesticide residues/Poisoning in India

In India the residues of pesticides in food, raw agricultural commodities and components of the environment have not so far been studied extensively. Yet a few reports show the presence of pesticide residues in essential commodities. Research in Tarai area of Uttar Pradesh shows an average DDT content of 0.46 ± 0.35 ppm in vegetables (Visweswaraiah, 1975). BHC levels in some vegetables in Mysore varied from 10.5 to 20 ppm. Research in Tarai area showed an average DDT content of 0.845 ± 0.51 ppm in dairy concentrates; 0.39 ± 0.028 ppm in poultry eggs, 0.58 ± 0.64 ppm in hay and other feeds and 0.0032 ± 0.002 ppm in milk (Visweswaraiah, 1975). Joia et al., (1979) reported contamination of BHC and HCH ranging from 1 to 5 ppm in wheat flour in Punjab.

The incident of pesticide poisoning in agricultural workers of Handigodu came to light in December, 1977; when they were reported to have suffered from
painful swelling and immobilization of hip and knee joints. Ultimately leading to
disuse atrophy of lower limbs, due to long term consumption of pesticide
exposed crabs and fish (NIN, 1977). The death of 150 persons in Kerala due to
the consumption of malathion mixed wheat has also been reported (The Hindu,
1985). Reddy (1985) reported that in the twin cities of Andhra Pradesh, many
women suffered with abortions and children showed chromosomal damage of
pesticide containing grapes. David (1985) has cited two epidemics of epilepsy in
Sitapur of Uttar Pradesh due to BHC poisoning.

A rapid survey conducted by the Central Fisheries Extension Centre,
Hyderabad revealed the mortality of large variety of fish during 1973 due to
pesticides (Hingorani et al., 1973). According to a report of Central Bureau of
Investigation (CBI), Government of India, as many as 4536 persons lost their
lives in 1965 alone on account of carelessness in handling poisonous substances
(Visweswaraiah et al., 1975).

Classification of Pesticides

Pesticides are classified into (i) Organochlorides; (ii) Organophosphates;
(iii) Carbamates; (iv) Synthetic pyrethroids.

i) Organochlorides: These insecticides as exemplified by DDT, endrin,
dieldrin and aldrin etc. are soluble in water and hence are the most persistent
compounds in the environment and are often referred to as “hard” pesticides. A
great deal of work has been done on these insecticides with reference to their
uptake of and persistence, environmental hazards and toxicological failure due to resistance in fishes.

ii) Organophosphates: These compounds were discovered during II World War by Gerhard Schroder, a German Chemist who was engaged primarily in the search for more powerful agents of chemical warfare (Bowen and Hall, 1952). The organophosphorus (OP) insecticides are esters of phosphoric acid. The first importance of insecticide, tetraethylpyrophosphate (TEPP) was primarily used as a substitute for nicotine against aphids. More stable OP insecticides such as parathion soon replaced it, and OP insecticides are now replacing it in turn with lower mammalian toxicity such as the malathion. The OP compounds are water-soluble systemic insecticides and they are less persistent in environment. Considerable amount of work has been done on the toxicity of these pesticides to fishes.

In insects, as in mammals they act by inhibiting the enzyme AchE that normally break down the neurotransmitter. The measurement of AchE activity is taken as a good indication of the pollution of aquatic environment by organophosphorus pesticides (Rainford, 1978; Koundinya and Ramamurthy, 1980 Nagarathna and Ramamurthy, 1983).

iii) Carbamates: These produce toxicity similar to that of organophosphates, but are less serve. One of the major differences is that carbamate-inhibited cholinesterases react more rapidly than the enzyme inhibited by organophosphates. With the result, the effect does not last as long as in case of
carbamate poisoning. However, an insecticidal carbamate aldicarb, is one of the few pesticides that has given raise to poisoning in consumers of treated food.

iv) Synthetic Pyrethroids: These are natural insecticides produced from interalia pyrethrum, a plant of the composite group and are esters of pyrethric (or) chrysanthimic acids. The synthetic pyrethroids are structurally similar compounds rendered photostable by various substituent groups, such as chlorine, bromine (or) cyanide on the basic structure. Some of the newer ones bear a more distant structural relationship to the pyrethrins. Because of their low mammalian toxicity, high insecticidal potency and lack of persistence in the environment, they have achieved widespread usage in agriculture, as household insecticides and in wood preservation. However, they are very toxic to aquatic organisms (Zitko et al., 1979) and their lack of persistence can be a problem when the synthetic pyrethroids are used as wood preservatives.

1.3 PYRETHROIDS

Pyrethroid insecticides are the synthetic analogous of naturally occurring pyrethrins from the flowers of Chrysanthemum species. These are considered as effective insecticides due to their high insecticidal toxicity with low mammalian toxicity (Elliot et al., 1974). The toxicity of these compounds was increased with the substitution of dihalovinyl containing acid moiety and with the esters of α-cyanophenoxy benzyl alcohol (Elliott et al., 1976). There are two types of mode of action of the pyrethroids based on the symptoms, produced. Type I syndrome was produced by pyrethroids without an α-cyano constituent, resulting in its action on the central and peripheral nervous systems, whereas Type II syndrome
was produced by compounds with an α-cyano group, resulting in its action only on the central nervous system (Barness and Verschoyle, 1974). However, both natural pyrethrins and synthetic pyrethroids are neurotoxicants, which act directly on excitable membranes and thereby interfere with membrane ionic conductance in target organisms (Wouters and Bercken, 1978).

The different doses of pesticides have different target sites of action through which they manifest their toxic effect. Many pesticides are reportedly metabolic stressors too. Hence, they have a secondary effect on the enzymes of glycolytic pathway.

Pyrethroids were three categories. (1) Pyrethrins, to present the parent insecticide, (2) Permethrin, cis-permethrin, trans-permethrin, resmethrin and tetramethrin to represent Type I compounds, having a phenoxy benzyl group, (3) Cypermethrin and deltamethrin to represent Type II compounds, having an α-cyanophenoxy benzyl group.

History

The effectiveness of natural pyrethrins in controlling a wide variety of insects led to the synthesis of several new related compounds. Allethrin, tetramethrin, kothrin, kadethrin, proparthrin and prothrin were early synthetic pyrethroids. All these compounds, although effective against several pest species failed to extend their range of application over natural pyrethrins and only limited use either due to high mammalian toxicity or due to their unstable nature in light and air. However several recent compounds e.g., permethrin S-5439, fenvalerate
cypermethrin, deltamethrin were developed by US and Japanese workers. These are not only active against a number of insect species, but are quite stable in light and oxygen, compared to natural and earlier synthetic pyrethroids, and exert prolonged residual action. These are used in large-scale cross protection. These compounds have very low toxicity to mammals and birds, but they are highly toxic to fish and their non-specific toxicity to insects may prove hazardous to bees and other beneficial insects.

The use of the pyrethroid, deltamethrin is to protect crops and health, through its toxic effects on harmful insects can be considered as safe for man, animals, fish and non-target fauna.

Deltamethrin is a photo stable pyrethroid providing valuable insecticidal activity against large number of pests - protection against insect pests in agriculture requires saltry not only for applicators, but also for non target living organisms in the wild and terrestrial fauna.

Synthetic pyrethroid insecticides are photostable analogs of the natural pyrethrins of botanical origin. Their structures range from very similar to the original (Ex. allethrin) to highly dissimilar compounds (Ex. flucythrinate). Directed synthesis by groups in Japan (Sumitome Chemical Co.) and England (NRDC) resulted in very potent insecticides and a commercial success for the synthetic pyrethroids. The physical properties of some synthetic analogous are also considerably different from their predecessors. Water solubility's of certain new derivatives are much lower (ex. 10 to 80 ppb) and lipophilicity is higher (Octanlar water partition coefficients of $10^5$ to $10^6$). Halogens present on some
synthetic pyrethroids (Ex. fenfluthrin) contribute to greater persistence, providing better residual activity against insects, but increase the potential for environmental effects as well. Rates of degradation by biological, chemical and physical agents are extremely different for the 3 representative pyrethroids. Most of the synthetic pyrethroids still retain at least 2 degradophores (Ex. carboxy ester, germinal dimethyl grup), but several highly halogenated compounds have long residual half-lives in the environment.

The synthetic pyrethroid is a function of intrinsic toxicity at the site of action, as well as the toxicokinetics that influence the deposition of the toxicant in the body, i.e., entry, distribution, elimination and biotransformation.

Chemistry of Pyrethroids

The pyrethrum extract contains six closely related insecticidal esters, collectively referred to as the pyrethrins, which differ only in terminal substituents in the side chains of the acid and alcohol components. The acid is substituted by chloropropane carboxylic acid and alcohol is substituted by cyclopentenolene. Generally three alcohols are involved, (1) Pyrethrolone, (2) Cinerolone and (3) Jasmolone for the Pyrethrins, Cinerins and Jasmolins respectively. The two acids involved are chrysanthemic acid for the I series and pyrethric acid for the II series (Casida et al., 1983).

The biological activities of the pyrethrum constituents depends on the structural and stereo chemical characteristics of both acid and alcohol components. Pyrethrin I and II are considerably more potent than the cinerins and jasmolins. The chrysanthemates are generally more potent for killing and the
pyrethrates for knocking down. The pyrethrins have three chiral centers and therefore eight different optical active isomers are possible. The geometrical isomerism in the side chain of the alcohol (Chrysanthemates) or of the acid and alcohol (Pyrethrates) gives the number of possible stereo isomers to sixteen for the chrysanthemates and 32 for the pyrethrates. Although these isomers have not all been prepared and tested, the available evidence strongly implied that the naturally occurring configuration is likely to be the most potent one (Casida et al., 1983). The effectiveness and stability have substantially increased with the substitution of a dihalovinyl containing acid moiety as in permethrin (Matsui and Yamamoto, 1971; Nelson and Somagyi, 1952) and the potency is further enhanced by the esters of α-cyano phenoxy benzol alcohol as in cypermethrin, deltamethrin, fenvalerate and fenpropathrin.

**Uses of Pyrethroids**

Pyrethroids are primarily used for the control of household, agricultural insect pests as well as in industrial, stored product and veterinary applications. In houses, restaurants, and air crafts and for preharvest treatment of expensive food crops and in public health (Stevenson, 1963). As film in heavy white oil they persist adequately in dark warehouses to control insect infestations of grain (Potter, 1935, 1938). Due to volatility as well as photostability different analogues of pyrethroids have found their application even in domestic mosquito soils (Maciver, 1963). In 1982, 30% of the world market of insecticides consisted of pyrethroids (Vijverberg et al., 1982) and this percentage has been increasing ever since.
The recent and more stable pyrethroids which are effectively harmless to mammals, birds and phyto toxic combine the high insecticide activity of the earlier pyrethroids with suitable persistence, so that they could be expected to control a broad spectrum of plant pests and particularly useful for crops such as cotton, which is severally attacked by a range of insect species Lepidoptera, which are potentially destructive pests on many dicotylendonous crops such as cotton, tobacco, apples, pears, plums, peaches, vines, oliver, soya, coffee and vegetables. In particular, insecticide is used exclusively throughout the world to protect cotton than any other crop. Field applications of some of the newer pyrethroids are reviewed by Ruscoe, (1977), permethrin (Breese, 1977), cypermethrin (Lhoster and Piedallu, 1977), decamethrin and related compounds (Breese and Searle, 1977).

The range of insects affecting cotton is not the same every where. Lhoster and Piedullu (1977) observed 14 species in West Africa, nearly all controlled by decamethrin. Similarly, pyrethroids are expected to control related pests of tobacco. In one study (Plapp and Venson, 1977) it was noticed that decamethrin was the only insecticide of 19 (3 organochlorine, 10 organophosphorus, carbonyl, chloradine form, natural pyrethrins, fenvalerate and permethrin) that was more toxic to tabacco bud worms. Synthetic pyrethroids are effective against the adult, larvae and egg stages not only of lepidopteraus, but also to many Coleoptera, Diptera and Heteroptera that cause economic damage to crops to fruit, oil seeds, grapes, soyabean and vegetables. Permethrin was used to control the oriental fruit moth, cydia mo lesta (Ruscoe, 1977), cadling
moth, *Lesperesiapomonella*, on apples (Hameed and Allen, 1976) with cypermethrin, knock down of various fruit pests.

Cypermethrin (Breese, 1977) and permethrin (Ruscoe, 1977) are very effective against the Colorado potato beetle, *Leptinotarsa decemlineata*. In addition to its action on active larvae, permethrin killed larvae as they emerged through treated egg shells into sprayed foliage. These compounds also control the diamond black moth, *plutellaty lostella* on cabbage, larvae on leaves treated with permethrin were not always killed directly, but starved until desiccated; the deposits persisted rain washing (Ruscoe, 1977). For some applications, special formulations of the pyrethroids are appropriate. Permethrin gave a higher mortality of large *Atta cephalotes* colonies (Phillips and Etheridge, 1977).

**Persistence of pyrethroids in the environment**

The environmental fate and degradation of pyrethroid insecticides has been reviewed (Roberts, 1981). Their compounds are all esters and microscopic organisms. Permethrin, one of the most widely used agricultural pyrethroids, has a half-life of one to three weeks in various silt and clay soils and upto 15 weeks in organic soils (Belenger and Hamilton, 1979; Williams and Brown, 1979, Chapman and Harris, 1981; Chapman *et al*., 1981). Cypermethrin, fenvalerate and fenpropathrin have half-life of approximately two to four weeks in mineral and organic soils (Chapman and Harris, 1981). Deltamethrin is more persistent with a half-life of more than two months in soils (Chapman *et al*., 1981).
Pyrethroid impact on non-target organisms

The biological activities of pyrethroids are intimately related with their chemical structure. The literature surveys on the effects of pyrethroids on the physiological and biochemical aspects insighted the following trends. The alterations in the larval development, larval metabolism, osmoregulation during osmotic stress may be indirectly related to the altered ionic transport processes when shrimp larvae were exposed to sub-lethal concentration of fenvalerate (McKenney and Hamarker, 1984). The effects of permethrin and deltamethrin on some biochemical effects of tribolium were studied in detail (Saleem and Shakoori, 1985a). They found that permethrin has elevated acid phosphatase activity and LDH while deltamethrin elevated alkaline phosphatases, amylase and A, AT and SDH. Fenvalerate exposed Daphnia species showed significant reduction in RNA (McKee and Knowles, 1986). The effect of permethrin on DNA, RNA and total proteins has also been reported in tribolium larvae (Saleem and Shakoori, 1985a). The studies on the effect of deltamethrin on glucose metabolism in Locust species revealed the increased conversion of P \((^{14}\text{C}_6)\) glucose in \(^{14}\text{CO}_2\) (Moreau et al., 1987). The sub-lethal effect of deltamethrin on glycemia, lipemia and gut alkaline phosphatase was reported in honey bees (Bounias et al., 1985).

*In vitro* studies on cultured human lymphocytes showed that fenvalerate and cypermethrin induced chromosomal structural aberrations (Puig et al., 1988). The reports of increased frequencies of micronuclei in cultured human lymphocytes (Surralles et al., 1990) as well as cultured Chinese hamster V-79
cells (Bakhitova et al., 1988) due to cypermethrin stand as good examples of the genotoxic nature of pyrethroids. Reduced levels of ATP were noticed in *Daphnia magna* exposed to fenvalerate (McKee and Knowles, 1986). Effect on Na\(^+\) - Ca\(^{2+}\) and Ca\(^{2+}\) - Mg\(^{2+}\) ATPase activities were studied in *Periplanata americana* by the two types of pyrethroids (Clark and Matsumura, 1987).

It was found that fenvalerate significantly reduced the oxygen consumption and also interferes with the enzymes of the oxidative metabolism such as SDH, MDH, and cytochrome in the prawn *Metapenaeus monoceros* (Srinivasulu Reddy et al., 1987). Inhibition of acetylcholinestarase activity due to cypermethrin in *T. mossambica* (Reddy et al., 1991) and in cockroach due to fenvalerate (Yelamma and Ravikumar Reddy, 1987) were reported. Deltamethrin caused hyperglycemia with slight change in lipid fractions and simultaneous operations of lipogenesis and lypolysis with a drop in phospholipid content during cypermethrin induced stress has been reported in *T. mossambica* (Reddy et al., 1991). The activities of catalase superoxide dismutase were also found to decrease during fenvalerate intoxication in *T. mossambica* (Radhaiah and Jayantha Rao, 1988). Disturbed protein metabolism in catfish, *Clarias batrachus* has also been reported due to acute toxicity of Decis (Ravindar, 1989) and in *T. mossambica* due to cypermethrin toxicity (Reddy et al., 1991). Impaired oxidation of carbohydrate with alterations in the pathways involved in CN were investigated in *T. mossambica* exposed to cypermethrin (Reddy et al., 1991). Inhibition of AchE and elevation of Ach content was studied in fresh water fish, *T. mossambica* treated with fenvalerate (Radhaiah and Jayanth Rao, 1988).
Yellamma and Ravikumar Reddy (1987) reported the inhibitory activity of AchE in ventral nerve chord of *Periplanata americana* under lethal and sub-lethal concentration of fenvalerate.

Studies relating to toxic impact of pyrethroids such as cypermethrin and fenvalerate LC$_{50}$/48 h for fenvalerate and cypermethrin have been determined for *C. carpio* (Malla Reddy, 1988). Both these pyrethroids were known to reduce the oxygen consumption in fresh water fish *C. carpio* (Malla Reddy, 1987). The studies on the effects of cypermethrin on carbohydrate metabolism of *Labeo rohita* indicated glycogenolysis leading to the elevated blood glucose level. Activity levels of SDH, LDH, MDH were also altered (Sridevi, 1992). Changes in blood profiles were noticed as a consequence of distorted haemopoietic tissue in *Cyprinus carpio* under cypermethrin intoxication (Malla Reddy and Basha Mohiddin, 1989). Inhibition of AchE with increase in Ach content (Malla Reddy *et al.*, 1992) and decreased activities of Mg$^{2+}$ and Na"/K" ATPase (Malla Reddy, 1988) were noticed in all tissues of *C. carpio* exposed to fenvalerate.
Table 1
Sources of pollutants entering different Indian rivers

<table>
<thead>
<tr>
<th>S.No</th>
<th>Name of the river</th>
<th>Mills</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Kali at Meerut</td>
<td>Sugar mills, distilleries, paint, soap, rayon, silk, yarn, tin and glycerin industries.</td>
</tr>
<tr>
<td>2</td>
<td>Yamuna in Delhi</td>
<td>DDT factory, sewage, Indraprastha power station, Auto mobile workshops.</td>
</tr>
<tr>
<td>3</td>
<td>Ganga at Kanpur</td>
<td>Jute, chemical, metal and surgical industries, textiles mills, tanneries and great bulk of domestic sewage of highly organic nature.</td>
</tr>
<tr>
<td>4</td>
<td>Gomati near Lucknow</td>
<td>Paper and pulp mills, sewage, soap.</td>
</tr>
<tr>
<td>5</td>
<td>Dajora in Bereely</td>
<td>Synthetic rubber factories, chemical mills, sewage.</td>
</tr>
<tr>
<td>6</td>
<td>Damodar between Bokaro and Panchet</td>
<td>Fertilizers pesticides flyash from steel mills, speeded coal particles from washeries and thermal power station.</td>
</tr>
<tr>
<td>7</td>
<td>Hoogly near Kolkata</td>
<td>Power stations, paper, pulp, jute textiles, chemical mills, paint varnishes, metal, steel hydro generated vegetables oils, soap polythene industries and sewage.</td>
</tr>
<tr>
<td>8</td>
<td>Sone at Dalmianagar</td>
<td>Cement, pulp and paper mills.</td>
</tr>
<tr>
<td>9</td>
<td>Tungabhadra</td>
<td>Pulp, oil, paper and steel industries.</td>
</tr>
<tr>
<td>10</td>
<td>Cooum, between Adyar and Beckingham canal</td>
<td>Domestic sewage and automobile work shops.</td>
</tr>
<tr>
<td>11</td>
<td>Cauvery (Tamilnadu)</td>
<td>Sewage, tanneries, paper, rayon and distillaries.</td>
</tr>
<tr>
<td>12</td>
<td>Godavari near Rajahmundry</td>
<td>Paper mills.</td>
</tr>
<tr>
<td>13</td>
<td>Siwan</td>
<td>Paper sulfurs, cement and sugar mills.</td>
</tr>
<tr>
<td>14</td>
<td>Kulu (between Bombay and Kalyan)</td>
<td>Chemical factories, rayon mills and tanneries</td>
</tr>
<tr>
<td>15</td>
<td>Suwao in Balarampur</td>
<td>Sugar industries.</td>
</tr>
</tbody>
</table>
Table 2
Liquid formulations sold in Andhra Pradesh

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Name of the pesticide</th>
<th>Formulation quantity in metric tons</th>
<th>Active ingredients in metric tons</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Monocrotophos 36% WAV</td>
<td>1,09,322</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Parathian 50% EC</td>
<td>1,39,615</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Demeton 25% EC</td>
<td>37,770</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Phosphonidon 85% (W/W)</td>
<td>1,00,165</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Endosulfan 35%</td>
<td>2,84,180</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Dimethoate 30%</td>
<td>2,59,376</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Malathian 50% EC</td>
<td>97,267</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Dichlorovos 76%</td>
<td>73,490</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Femirothion 25%</td>
<td>4,152</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Quinolphos 20% EC</td>
<td>20,6761</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Chloropyrifos 35%</td>
<td>29,4130</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>Phosolone 20% EC</td>
<td>17,885</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>Diazine 20%</td>
<td>83</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>Synthetic pyrethroid, Decamethrin, fenvalerate</td>
<td>18,390</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>Others</td>
<td>14,692</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>17,89,902</td>
<td></td>
</tr>
</tbody>
</table>
Table 3

Pesticide contamination to man
(Subramanyam and Sambamurty, 2000)