# Review of Literature

Global environmental perturbations affecting the biodiversity and production functions of all kind of ecosystems. In recent years the alarm of environmental degradation has attracted the attention of experts and planners alike and they have been surrounded by a volley of questions: What resource has been affected? How large area has been affected? What caused it? What can be done to cope with the situation? The effective answers rest with viewing the problems in its totality as the process of environmental degradation is mainly a function of various anthropogenic activities and is transboundary in nature. To be precise it is a period of rapid change in population, economy and environment, increasing gap between rich and poor, and increasing disequilibria between the growth and the capacity of the environment to sustain it. It was however agreed in Agenda 21 of the Rio Conference in 1992 about a new concept of resource management, the so-called "sustainable development". It has, of late, been realized that development that meets the needs of the present without compromising the ability of future generations to meet their own needs should be the key issue of development in order to protect the environment from a total collapse.

## Aquatic Pollution: Overview

The aquatic ecosystems acting as the ultimate sinks of almost all environmental aberrations, can be the mirrors of environmental degradation following various anthropogenic activities. The drainage basins as a whole and the rivers in particular are being devastated by intensive human activities. River Ganga, the life- line of cultural ethos for instance, has brutally been assaulted to the extent that, barring the region around head water, it has almost lost its originality in terms of ecological intricacies.

The inland aquatic resources are highly threatened due to indiscriminate dumping of industrial wastes, domestic sewage, agricultural run-off and soil erosion (Jhingran, 1991). Thus not only rivers but also other water bodies such as ponds, lakes and reservoirs have been converted into a receiving pot for all kinds of waste, which in turn have vitiated the water quality and biota to the extent of irrepairable state.

The gradual accumulation of toxic substances, heavy metals, pesticides and non-biodegradable chemicals in particular, besides unabated organic loading in the system have assumed serious proportion as the danger of their entry into human body is lurking large.

Environmental pollution by heavy metals is instantly recognized with the Minamata disaster in Japan, when several thousands of people suffered mercury pollution by consuming the oysters caught in the Minamata bay which was the recipient of mercury released from a vinyl chloride plant between 1953 and 1960 (Smith and Sandifer, 1975). Similarly, the level of cadmium in local food stuff in parts of Japan, attributed to irrigation water from the soil heaps of an abandoned mine, caused Itai- Itai Bye disease in 1955, mainly in women over forty (Moore, 1990). Thus the heavy metals may be speedily transferred the ambient environment into the food chain (Adema *et al.*, 1972).

Eutrophication is also a type of pollution affected due to excessive loading of organic matter only which has all the potentialities to upset the ecological balance of an ecosystem, as observed in case of floodplain lakes in the Ganga and the Brahamaputra basins (Sinha and Jha, 1997 a, b).

Although sewage is rich in nutrients, nevertheless, it may pose problems to the sewage-fed biotic produces by being toxic to them directly or to their natural foods due to its physico-chemical characteristics (high BOD, low $O_2$ tension, suspended solids etc.). Further bioaccumulation of pesticides, heavy metals, detergents may occur in the biotic produces of sewage-fed system (Buras, 1988) and the wide use of pesticides in agriculture has become a pervasive threat to many natural aquatic ecosystems.

## Pesticides: One of the prime aquatic pollutants

### *Environmental transport*

There are several routes for pesticides to enter aquatic environments, including spillage, inappropriate disposal of dilute pesticides and washing of equipment used for application, run-off and leaching from the agricultural field and through drainage tiles (Torstensson, 1989). Other possibilities are transportation by wind drift when applying the pesticides and through volatilization of pesticides from soil and vegetation after application (Kreuger, 1999). Pesticides in the atmosphere can then be transported to and deposited on surface waters

(Figure 1). In summary, the main transportation routes of pesticides from the field to surrounding waters are volatilization/deposition, run-off and leaching (Kreuger, 1999). Rainfall and irrigation affect the intensity of the two latter.

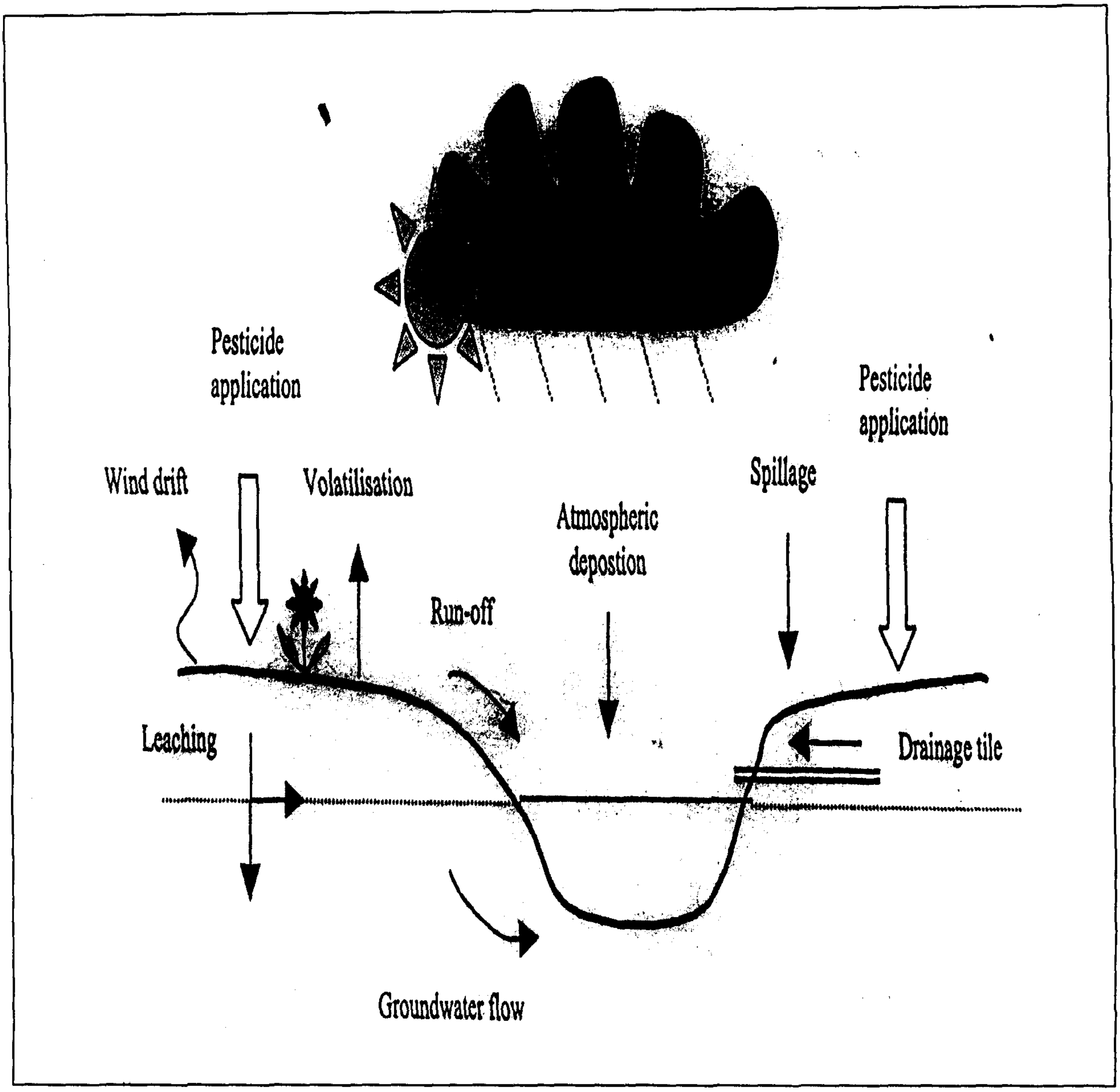


**Figure: 1 Possible routes for pesticides used in agriculture to enter surface water and groundwater. Modified after Kreuger (1999)**

## *Bioaccumulation*

Bioaccumulation is the general term describing the net uptake of chemicals (usually nonessential ones) from the environment by any or all of the possible routes (i.e., respiration, diet, dermal) from any source in the aquatic environment where chemicals are present (i.e., water, dissolved, colloidal or particulate organic carbon, sediment, other organisms) (Spacie *et al.*, 1995). Bioaccumulation is of concern both for its possible effect on the organism and for the contamination of higher trophic levels, including humans that may occur. The widespread use of pesticides for more than four decades has resulted in problems caused by their interaction with natural biological systems. The complex inter-relationship of these systems has been illustrated in figure 2 (David *et al.*, 1993).

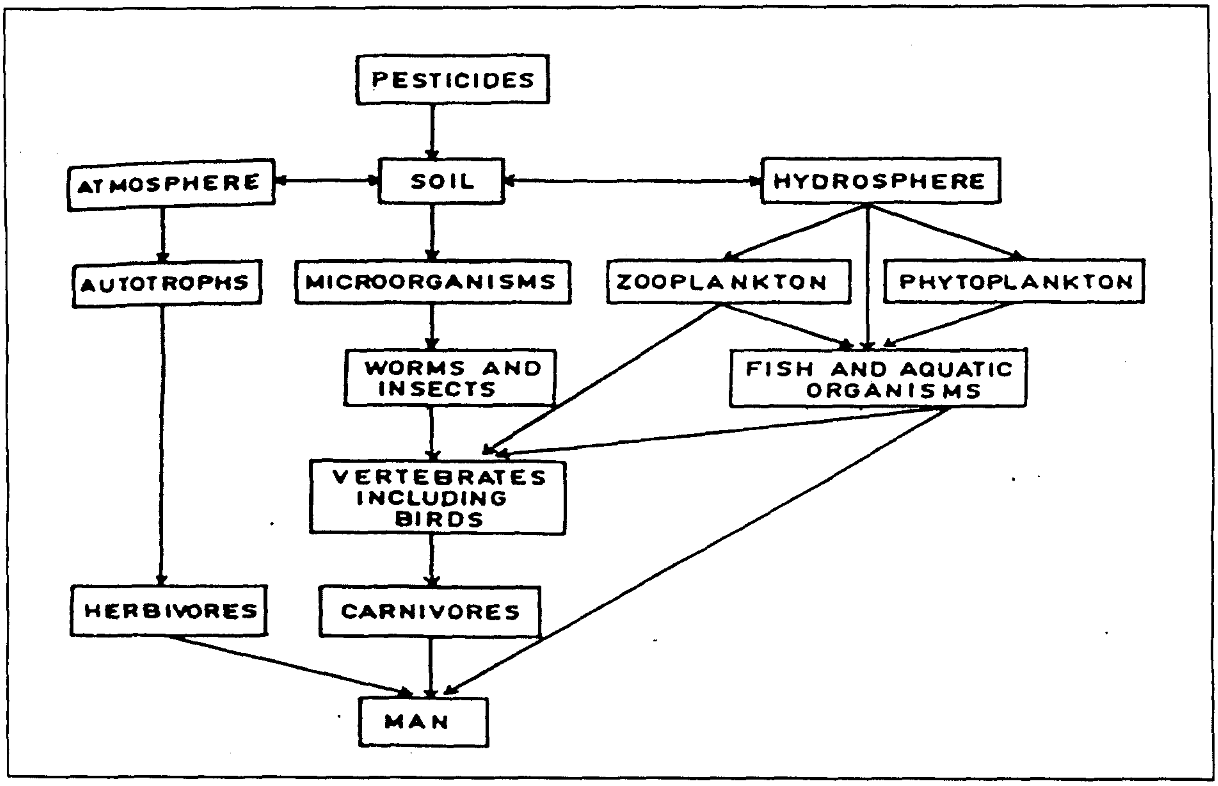


**Figure: 2 Schematic diagram of biological transfer of pesticides to man**
**(David *et. al.*, 1993)**

Non-polar compounds with high hydrophobicity, e.g. PCBs and DDTs, tend to accumulate in organisms. Unlike organochlorine pesticides, which are long-lived in the environment and cause biological damage when they accumulate in an organism's system over time, OP and carbamate pesticides are short-lived in the environment and fast acting on their "target pest." Direct mortality of wildlife from organochlorine pesticides was uncommon (Hayes and Wayland, 1975); however, mortality is the primary documented effect on wildlife from OP and carbamate pesticides (Grue *et al.,* 1983). Organophosphorus and carbamate pesticide toxicity is not specific to a target "pest," and lethal effects are seen in nontarget organisms. Generally speaking, newer pesticides are much less persistent and less likely to bioaccumulate than earlier organochlorine pesticides, such as DDT, and organophosphate pesticides, such as parathion. Generally, these characteristics coincide with long biological half-life and they tend to bioaccumulate and possibly biomagnify in a food web. Bioaccumulation can be expressed by the bioconcentration factor (BCF), which is the ratio between the concentration in the organism and its food or the ambient medium. Bioaccumulation is affected by the rate of transformation/degradation of the compound in the organism.

Biomagnification of a compound means, that it is present at increased levels in organisms representing higher trophic levels in the food web. Organisms in aquatic ecosystems may take up pesticides from the food and ingested water, but a diffusion of pollutants between the organisms and the ambient water is also possible (Walker *et al.*, 1996). Differences in feeding, living habits and trophic level of fish can affect their exposure to pollutants like pesticides. Predatory fish may accumulate hydrophobic compounds by eating other organisms, while bottom feeders are in constant contact with pesticides sorbed to the sediment. Herbivorous fishes grazing phytoplankton and periphyton also have a close contact with the sediment. Cullen and Connell (1992) found, that the concentration of dieldrin and DDT with metabolites increased with the age of the fish in an Australian river as a result of bioaccumulation and bioconcentration. A number of workers have investigated the toxicity, uptake and tissue distribution of pesticides in a number of fishes (Anderson and Defoe, 1980; Guiney and Peterson, 1980; Tilak *et al.*, 1980). Because they are generally designed to be persistent pesticides, their residues and breakdown products can remain in the environment for long periods. Because they are also designed to affect living organisms, they may accumulate in flesh and their impacts may be magnified as they are transferred up the food chain. The air breathing fish, *Channa punctatus* inhabiting the accumulated water in the paddy field besides ponds, are the worst sufferer of residual effect of organophosphate pesticides (though lower persistent) as revealed from some earlier records of investigation (Akhtar, 1984; Sun *et al.*, 1999; Carr *et al.*, 1997).

The poisoning by pesticides from agricultural fields is a serious water pollution problem and its environmental long-term effect may result in the incidence of poisoning of fish and other aquatic life forms. From adjoining crop fields pesticides are drained into ponds (Konar *et al.*, 1997), resulting in depletion in fish yields. Pesticides have been recognized as serious pollutants of the aquatic ecosystem with drastic effects on aquatic fauna. (Sharma *et al.*, 1982; Pal and Konar, 1985; Mani and Konar, 1986; Holden, 1973). Several pesticides are known to reduce growth and fecundity of fish and many invertebrates (Johnson, 1968; McKim *et al.*, 1974.). Poisons are known to affect physico-chemical parameters of water, which ultimately affect the fish (Singh, 1998). Although pesticides produce good many results in the control of pests, their harmful effects on the non-target animals can not be ruled out. Pesticides leave residues in water and mud even several days after their spray in the adjacent crop field. This poses a constant threat to the non-target organism especially to the fishes, because pesticides are known to alter their behaviour pattern (Anderson, 1971), growth and nutritional value (Arunachalam *et al.*, 1980; Yaganobano and Tariq, 1981) and total erythrocyte count (TEC) (Mukhopadhyay and Dehadrai, 1980). Pesticides may affect estuarine microorganisms via spills, runoff, and drift. detrimental effects of pesticides on microbial species may have subsequent impacts on higher trophic levels. Both the structure and the function of microbial communities may be impaired by pesticide toxicity (DeLorenzo *et al.*, 2001). The ecological effects on aquatic organisms caused by pesticides in surface water are dependent both on the peak concentrations the pesticides may reach and the duration of exposure of organisms to pesticides. High concentrations of pesticides can cause acute effects on biota even at a short duration, while low concentrations at long duration may cause chronic effects. If treatment of fields with pesticides coincides with rainfall and subsequent run-off events, high concentrations of pesticides may be found in surface water recipients. This may give adverse affects on sensitive populations of vertebrates such as fish.

India is considered one of the richest countries in the world with regard to its vast and varied freshwater resources. These aquatic resources are facing the problem of over- exploitation, as a result of which the required niche for the proper development of fish and fisheries has been hampered. So, not only the appropriate water management (Boyd, 1982) but also the agricultural management is very important for sustainable aquaculture development. Keeping in mind the detrimental effects on non-target aquatic resources, rational use of pesticides should be the prime focus of agricultural management

## Toxicity:

Toxicity is a relative property reflecting a chemical's potential to have a harmful effect on a living organism. It is a function of the concentration and composition/properties of the chemical to which the organism is exposed (i.e., externally and internally) and the duration of the exposure (Rand *et al.*, 1995). Toxicity can be divided into the broad categories direct and indirect. Direct toxicity results from the toxic agent acting more or less directly at sites of action in and/or on organisms; indirect toxicity occurs as a result of the influence of changes in the chemical, physical, and/or biological environment (e.g., changes in the quality and/or quantity of food organisms or habitat changes and/or losses).

Aquatic toxicity test methods may be categorized according to length of exposure, test situation, criteria of effects to be evaluated, and organisms to be tested. Chronic toxicity tests permit evaluation of the possible adverse effects of the chemical under conditions of long-term exposure at sublethal concentrations. (Rand *et al.*, 1995). Chronic exposure typically induces a biological response of relatively slow progress and long continuance. The chronic aquatic toxicity test is used to study the effects of continuous, long-term exposure to a chemical or other potentially toxic material on aquatic organisms.

In the aquatic environment organisms are not usually exposed to high, acutely toxic concentrations of chemicals unless they are restricted to the vicinity of a chemical release site or spill area. Beyond the initial impact site, dilution and dispersion occur, decreasing these acute concentrations to lower, potentially sublethal levels. In general, a grater biomass is exposed to sublethal concentrations of chemicals than to acutely toxic lethal concentrations. The lower concentrations may not produce death, but they may have a profound effect on the future survival of the organisms.

Sublethal effects may be studied in the laboratory by a variety of procedures. Such effects generally are divided into three classes: biochemical and physiological, behavioral, and histological (Sheehan *et al.*, 1984). Biochemical and physiological effects tests include studies of proteins (e.g., enzyme inhibition, stress proteins), clinical chemistry, hematology, and respiration. Behavior represents an integrated response corresponding to complex biochemical and physiological functions, so chemically induced behavioral changes may reflect effects on internal homeostasis. Behavioral end points may thus be sensitive indicators of sublethal effects. Behavioral effects that have received considerable attention in aquatic organisms are locomotion and swimming, attraction-avoidance, prey-predator relationships, aggression and territoriality, and learning. These are all ecologically significant behaviors (Rand, 1985).

## Organophosphate Toxicity:

The air breathing fish, *C. punctatus* inhabiting the accumulated water in the paddy field besides ponds, are the worst sufferer of residual effect of organophosphate pesticides as revealed from some earlier records of investigation (Ghosh and Konar, 1973; Lal and Vohra, 1974; Thomas and Murthy, 1975; Anees, 1978 a b; Dubale and Shaw, 1978; Shafi and Akhtar, 1979, 1982; Akhtar, 1984). These insecticides have also been found to be toxic to algae. (Orus *et al.*, 1990; Marco *et al.*, 1990). Studies pertaining to the effects of pesticides on protein content and nucleic acid levels have been recorded. Dichlorovos (DDVP) reduces the nucleic acid levels and protein content in fresh water fish, *Tilapia mossambicus* (Peters), especially in brain, liver and muscles (Rath and Mishra, 1981) and thus in comparison to control fish a great loss in DNA, RNA and protein contents is observed in treated fish. In a study with piscine organs the protein quality reduced in both liver and kidney due to exposure of organophosphate pesticides (Awasthi *et al.*, 1984).

The quality of protein is dependent on the synthesis of RNA. Ansari *et al.*, (1988) studied diazinon toxicity in zebra fish exposed for 24 hours to 168 hours and showed a significant time dependent effect on the nucleic acid and protein content. Anees (1974) studied serum protein change of a fresh water teleost, *Channa punctatus* (Bloch), exposed to organophosphate insecticides. Phosphatase activities have been reported extensively in the liver of *Channa gachua* (Dalela *et al.*, 1978). Generally alkaline phosphatase activities in the liver and the muscle increase at lethal concentration and decrease at sublethal concentration in the fish, *Channa sp.* exposed to thiodon and rogor (Verma *et al.*, 1982). Meteleve (1972) studied the effect of dimethoate, methyl nitrophos (MNP) on the carp and found that MNP intoxication increases the blood sugar level and causes the decrease in the glycogen content of the liver. Sublethal concentrations of malathion, an organophosphate insecticide, caused haematological and histopathological damage to channel catfish *(Ictalurus punctatus)* (Areechon and Plumb, 1990).

Deformities were found in the vertebrae and blood samples showed increases in numbers of erythrocytes and decreases in numbers of leucocytes. Jeney and Jeney (1986) also reported a rise in hematocrit levels after high-dose (2500 mg/l) treatment with trichlorphon, an organophosphate used in fisheries for control of planktonic invertebrates and certain parasite infections. The organophosphorus pesticide, sumithion, produced different physiological changes in the fresh water teleost, *S. mossambicus* (Peters) when exposed to a lethal concentration ($LC_{50}$, 6mg/l) for 48 hr. It was also found that exposure to sumithion depressed tissue respiration and inhibited citric acid cycle enzyme succinic dehydrogenase (SDH) activity. The glycolytic enzyme lactic dehydrogenase (LDH) was increased in sumithion exposed fish suggesting operation of anaerobic glycolytic pathway. Similarly, changes in blood glucose, muscle, liver glycogen content, phosphorylase activity were found. Alkaline phosphatase activity of *S. moassambicus* showed a rise in all tissues (brain, gill, muscle, liver, intestine, kidney) following exposure to sumithion (Koundinya and Ramamurthi, 1982). Sub lethal concentration of dimecron caused conspicuous pathological changes in the liver like

vacuolation of the cytoplasm of hepatocytes, enlargement of nuclei rupture of the cell membrane, liver cord disarray, damage of connective tissue, infiltration of phagocytes and necrosis (Sastry and Malik 1979). Catalase activity in liver and kidney are reduced remarkably by the action of phosphamidon. So the phosphamidon is a partial inhibitor of the enzyme catalase (Thomas and Murthy, 1976).
The rate of oxygen uptake of the bivalve depressed by the sub lethal levels of dimecron (Kulkarni and Keshavan, 1989). Organophosphate pesticides inhibit the acetylcholinesterase activity and also induces changes characteristic of " oxidative stress" (Hai *et al.*, 1997). Saleha Banu (2001) studied the genotoxic effect of monocrotophos and showed that the pesticide induced DNA strand breaks in *T. mossambica* in vivo. The genotoxic potential of methyl parathion and phosphamidon, two commercial formulations of organophosphorus pesticides, was evaluated through induction of sister chromatid exchanges (SCE) and chromosome aberrations in fish gill tissues (Das and John, 1999).

Phosphamidon appears to affect the principal cells of caput epididymidis indirectly through its toxic effect on the Leydig cells and the clear cells of the cauda epididymidis appear to be directly vulnerable to the toxic action of the pesticide (Akbarsha and Sivasamy, 1998). In vitro administration of chlorpyrifos-ethyl resulted in the induction of erythrocyte lipid peroxidation and significant changes in antioxidant enzyme activities (Gultekin *et al.*, 2000). Chlorpyrifos also interferes with brain development, in part by multiple alterations in the activity of transcription factors involved in the basic machinery of cell replication and differentiation (Crumpton *et al.*, 2000)

The long term and repeated administration of novel phosphorothionate caused significant increase of Acid (AcP) and Alkaline Phosphatases (AkP) in serum and kidney (AcP), whereas, these enzymes simultaneously decreased significantly in liver, kidney (female rat AkP) and lung tissues in both male and female rats after 45 and 90 days of treatment (Rahman *et al.*, 2000). The acute toxicity of two organophosphorus pesticides, diazinon and malathion to *Cyprinus carpio* and *Barilius vagra* was revealed from the study of (Alam and Maughan, 1993). Elumalai *et al.*, (1999) investigated the impact of monocrotophos on protein and carbohydrate metabolism in different tissues of albino rats and showed that the protein content decreased in muscle and kidney after treatment with monocrotophos. Due to their reputation for low environmental persistence, OP pesticides are often used indiscriminately resulting in detrimental exposure to humans and other nontarget species. Poovala *et al.*, (1998) hypothesized, that oxidative stress may play a role in the pathogenesis of acephate (AT)-induced acute tubular necrosis and renal dysfunction observed in cases of AT overdoses. A gradual decrease in muscle glycogen and an increase in lactate contents were observed in rogor exposed Indian catfish (Begum and Vijayaraghavan, 1999)

There is great concern about the use of pesticides for agriculture, silviculture, and public health protection (FAO, 1986). Sublethal levels of pesticides may accumulate in fish from the water or food. As by their nature, these diverse groups of toxic chemicals are often persistent in the environment and leach into the aquatic ecosystems, effects of pesticides and their breakdown products on fish need to be thoroughly investigated. Pesticides may act strongly on fish populations by indirectly affecting food chains. The Government of India has laid special emphasis on the adoption of Integrated Pest Management (IPM) strategies with a view to reduce the load of pesticide application in the crop eco-system by restoring to need-based application based on ETL (economic threshold level) of the target pest species. The major thrust thus lies in decreasing the pesticide load by substituting with readily degradable or 'soft' pesticides such as the organophosphates, carbamates, pyrethroids, etc. Even among these newer compounds the time has come to review and identify among them compounds, which are relatively environment friendly (REF) and fit into an IPM approach. At the same time, the wide spread use of organophosphate pesticides in agriculture and forestry conservation programs has prompted the need for evaluation of the hazards of such materials to wildlife and also non-target organisms.

Though the acute and sub acute toxicities of certain pesticides primarily the chlorinated hydrocarbon, then the organophosphate pesticides, have been investigated in several species of fishes, studies on the sublethal concentrations of organophosphorous toxicants are meagre. Two organophosphate pesticides, phosphamidon (Dimecron) and Quinalphos are selected for present toxicity study as they are most commonly used for management of insect pest of field crop and tea plantation in India especially in the state, West Bengal

# General properties of Phosphamidon and Quinalphos

## PHOSPHAMIDON

| | |
|---|---|
| COMMON NAME | PHOSPHAMIDON |
| CHEMICAL NAME | 2 - CHLORO - 2 - DIETHYLCARBAMOYL - 1 - METHYLVINYL DIMETHYL PHOSPHATE. |
| EMPIRICAL FORMULA | $C_{10}H_{19}CLNO_5P$ |
| MOLECULAR WEIGHT | 299.69 |
| PHYSICAL STATE | REDDISH BROWN VISCOUS LIQUID |
| SOLUBILITY IN WATER | IT IS MISCIBLE IN WATER. |
| SOLUBILITY IN ORGANIC SOLVENTS | MISCIBLE IN MOST ORGANIC SOLVENTS EXCEPT SATURATED PARAFFINS. ITS SOLUBILITY IN HEXANE IS 3.2 % AT 25 $^0$C. |

## QUINALPHOS

| | |
|---|---|
| COMMON NAME | QUINALPHOS |
| CHEMICAL NAME | O,O DIETHYL O - 2 - QUINOXALINYL PHOSPHOROTHIOATE |
| EMPIRICAL FORMULA | $C_{12}H_{15}N_2O_3PS$ |
| MOLECULAR WEIGHT | 298.3 |
| PURITY PERCENTAGE | 70 % MINIMUM |
| PHYSICAL STATE | THE PURE PRODUCT IS COLOURLESS CRYSTALLINE SOLID. |
| SOLUBILITY IN WATER | IT IS MISCIBLE IN WATER. |
| SOLUBILITY IN ORGANIC SOLVENTS | SOLUBLE IN METHANOL, ETHANOL, ETHER, KETONES, AROMATIC SOLVENTS. |