CHAPTER I

INTRODUCTION

1.1 AQUATIC POLLUTION: A BRIEF OVERVIEW

Freshwater is vital to life yet its environment is frequently being treated with greatest carelessness in terms of pollution. Pollution of Indian freshwater has become a major concern these days with rapid rise in hazardous chemicals in the aquatic environment. Massive deforestation and industrialization are destroying natural waters by adding effluents and wastes into it (Sabata and Nayar, 1987). Of particular cause of concern is the occurrence of heavy metals (Huang et al., 1997; Adham et al., 2002; Olojo et al., 2005) and pesticides which are rapidly discharged into water bodies as wastes and agricultural run-off. The reports of pollution of Indian rivers by some investigators like Ghose and Sharma (1988), Mahajan (1988), Mishra and Saksena (1991), Palharya and Malviya (1988), Trivedy and Goel (1986), Kudesia (1990), and Abbasi et al., (1996) are noteworthy.

Heavy metals are metals with a density at least five times that of water. As such, they are stable elements that cannot be metabolized by the body and hence are bio-accumulative and inhibit biological processes. Some heavy metals such as Co, Cr, Fe, Mn, Mo, Ni, Se, Sn, V and Zn are essential for growth, while some others like As and Ba may have possible beneficial uses. To be able to normally develop and function, an organism needs these minerals. Metals like Bi, Cd, Hg, Pb and Ti appear to have no apparent metabolic function and so are termed non-essential elements (Underwood, 1971). A deficit or an excess of one or more microelements may disturb the organism's internal equilibrium (Harper et al., 1983). The metal burden is augmented by human wastes and discharges. Studies by the Environmental
Protection Agency (Fundação Estadual de Proteção Ambiental - FEPAM) in Brazil's southernmost state, Rio Grande do Sul, revealed high loads of domestic and industrial sewage in the lower reaches of the Rio dos Sinos (FEPAM, 1999). Heavy metal pollution in an aquatic environment has been a matter of great concern as these are persistent chemicals with relatively long half life that do not break down readily. Heavy metals may affect organisms directly by accumulating in their body or indirectly by transferring to the next trophic level (Unlu and Gurgum, 1993; Miller et al., 2002; Censi et al., 2006). They cause serious impairments in metabolic, physiological and structural systems when present in high concentrations (Javed, 2003), influence behaviour by impairing mental and neurological function, neurotransmitter production and utilization, and altering numerous metabolic body processes. Systems in which toxic metals can induce impairment and dysfunction include the blood and cardiovascular, endocrine (hormonal), enzymatic, gastrointestinal, immune, nervous (central and peripheral), reproductive, and urinary (Garry, 2001), as well as detoxification (colon, liver, kidneys, skin) and energy production pathways. Many metals listed as environmentally hazardous are essentially dietary heavy metals required for normal growth and development of living organisms. They pose threat to organisms and ecosystems when they accumulate at concentrations beyond certain threshold values.

It will, thus, be interesting to see how an essential (Copper) and a non-essential (Cadmium) heavy metal affects an organism, especially when works of Gupta (1998b) showed high levels of heavy metals in sediments and water from Barak Valley. Hence, Copper and Cadmium were considered in the present research.

Agriculture is the lynchpin of the Indian economy. Ensuring food security for a population of more than 1 billion Indians with diminishing cultivable land resource is a herculean task. It is estimated that India approximately loses 18% of its crop yield valued at Rs.900 billion due to pest attack each year. The use of pesticides can help to reduce the crop losses, provide economic benefits to farmers, reduce soil erosion and help in ensuring food safety and security for the nation. A pesticide is any chemical which is used by man to control pests. The pests may be insects, plant
pathogens, fungi, weeds, nematodes, snails, slugs, etc., which in turn are controlled by insecticides, fungicides, herbicides, nematicides, etc. Under United States law, a pesticide is also any substance or mixture of substances intended for use as an insect or plant growth regulator, insect mating disruptor or egg sterilant, defoliant, or desiccant. Pesticides can be Bactericides, Fungicides, Herbicides, Insecticides, Molluscsicides, Nematicides, Rodenticides or Viricides, named after their primary target group. India is nearly self-sufficient in its pesticide requirement, with around 95% of requirements being met by local production. The country manufactures more than 90,000 metric tonnes (MT) of pesticides annually, ranking first in Asia and 12th in the world. The Indian pesticide industry has a turnover of more than 4.5 billion US dollars and an annual growth rate of 2–5%. The agricultural sector consumes about 67% of the pesticides produced; the remainder being used in public health programs. Within the agricultural sector, a few crops like cotton, paddy, vegetables, and fruits account for two-thirds of pesticide consumption. The consumption pattern of pesticides in India is also very different from the rest of the world. In India insecticides account for 76% of the total domestic market while herbicides and fungicides have a significantly higher share in the global market. In India, 381 grams of pesticide per hectare of cultivable land is used annually. There are wide regional variations in annual pesticide consumption throughout India. In the year 2000–2001, the states of Haryana, Punjab, and Uttar Pradesh consumed more than 5,000 MT. The states of Andhra Pradesh, Gujarat, Karnataka, Kerala, Madhya Pradesh, Maharashtra, Rajasthan, Orissa, and Tamil Nadu consumed between 1,000 and 5,000 MT. Assam, Bihar, and Himachal Pradesh consumed between 100 and 1,000 MT of pesticides, while Arunachal Pradesh, Jammu and Kashmir, Manipur, Mizoram, Nagaland, Tripura, Delhi and the union territory (UT) of Pondicherry consumed between 10 and 100 MT. Goa, Meghalaya, Sikkim and Union Territories viz., Andaman and Nicobar Islands, Chandigarh, Dadra and Nagar Haveli, Daman and Diu, and Lakshadweep ranked the lowest with a consumption of less than 10 MT (Dhaliwal and Singh, 2000). Though the application of pesticides is based on their toxicity to selective pests, it is not specific, resulting in very hazardous effects, particularly on aquatic organisms since pesticides eventually reach aquatic ecosystems in considerable
amounts as agricultural run-off from land, contaminated groundwater, bottom sediments, urban run-off, and outputs from municipal water treatment and manufacturing plants.

The pesticides normally used for plant protection and for destroying vector-borne diseases are categorised into 3 major groups based on the reactive groups present in the original molecule. These are: Organochlorine (OC), Organophosphate (OP) and Carbamate (Rao, 1999). In a survey made in Barak Valley, South Assam, covering five circles and three districts (Cachar, Karimganj and Hailakandi), it was found that among all pesticides, Endosulfan, an organochlorine and Malathion, an organophosphate, were mostly used in tea plantations and paddy fields, respectively. Both Endosulfan and Malathion was, therefore, chosen as test pesticides in the present study. Primary data from tea garden workers and various seed houses were collected and are tabulated below:

Table 1.1. (i): Survey of various tea estates, crop fields and seed houses for commonly used pesticides

<table>
<thead>
<tr>
<th>Tea estate</th>
<th>District</th>
<th>Area under cultivation (in hectares)</th>
<th>Pesticide used</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Tea</td>
</tr>
<tr>
<td>Rosekandy TE</td>
<td>Chuttabeel Circle, Cachar</td>
<td>570.11</td>
<td>Thiodan, Malathion, Endocid, Thimul, Thifor, Devicon, Cyclodan, Devicyper, Cypermethrin</td>
</tr>
<tr>
<td>Silcoorie TE</td>
<td>-Do-</td>
<td>459.0</td>
<td></td>
</tr>
<tr>
<td>Urrunaband TE</td>
<td>Happy valley Circle, Cachar</td>
<td>338.67</td>
<td></td>
</tr>
<tr>
<td>Chandighat TE</td>
<td>-Do-</td>
<td>550.70</td>
<td></td>
</tr>
<tr>
<td>Coombergram TE</td>
<td>-Do-</td>
<td>316.38</td>
<td></td>
</tr>
<tr>
<td>Doloo TE</td>
<td>North Cachar Circle</td>
<td>825.13</td>
<td></td>
</tr>
<tr>
<td>Aenakhal TE</td>
<td>Hailakandi</td>
<td>661.30</td>
<td></td>
</tr>
<tr>
<td>Isabeel TE</td>
<td>Longai Circle, Karimganj</td>
<td>573.21</td>
<td></td>
</tr>
</tbody>
</table>

Source: SVBITA, Centenary Souvenir, 2001
FIG 1.1. (i): Commonly used pesticides in paddy/other crops of Barak Valley

FIG 1.1. (ii): Commonly used pesticides in tea plantation of Barak Valley
1.2 TEST FISH/ MODEL OF STUDY

*Esomus danricus* is an active teleost species belonging to subfamily Rasborinae that inhabits shallow streams, floodplains, wetlands etc. of NE India.

*Esomus danricus*, a Danionin, is also known as the **Indian Flying Barb** owing to their extremely long barbels and an exceptional ability for jumping. *Esomus danricus* - first described in 1822 - is a silver-coloured fish with a black line on an elongated body and golden-tinged fins. Exceptionally long barbels reach almost to the anal fin (**Plate1**).

**Plate1**: *Esomus danricus*

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**DISTRIBUTION**

*E. danricus* is found in North, East and Northeast India, in the Himalayan foothills, Bangladesh, Malaya, Nepal, Pakistan, Srilanka, Thailand and South Vietnam.

**FEATURES**

Body of *Esomus danricus* is elongate and strongly compressed with rounded abdomen. Head and snout blunt. Mouth small, obliquely directed upwards, without symphyseal knob. Eyes placed inferiorly, visible from below ventral surface. Lips thin. Lower jaw is prominent. Two pairs of barbels present, maxillary pair very long
extending up to anal fin. Pharyngeal teeth present in a single row. Dorsal fin inserted in the interspace between anal and pelvic fins, nearer anal fin than pelvic, with six branched rays and no spine. Anal fin with five branched rays. Caudal fin forked. Scales are of moderate size. Lateral line absent or nearly so, piercing only four to six scales anteriorly. 14 scales around caudal peduncle (Jayaram, 1999). Approximately 20 species found in this genus: *E. ahli*, *E. altus*, *E. barbatus* (South Indian Flying Barb), *E. caudicellatus*, *E. dancria*, *E. dancricus*, *E. barbatus*, *E. danrica grahami*, *E. danrica thermoicos*, *E. danricus* (Flying Barb), *E. danricus jabalpurensis*, *E. lineatus* (Striped Flying Barb), *E. longimanus* (Mekong Flying Barb), *E. malabaricus*, *E. malayensis* (Malayan Flying Barb), *E. danricus*, *E. manipurensis*, *E. metallicus* (Striped Flying Barb), and *E. thermoicos* (Flying Barb).

Maximum length: 6 inch (15 cm)

Colour: silver

Temperature preference: 20-25°C

pH preference: ~7.6

Hardness preference: Soft and medium

Salinity preference: Zero

Life Span: 3-5years

Compatibility: Needs plenty of space, fast moving, maintenance moderate.

Feeding Habit: Surface feeder, prefers insects, can sustain on artificial food.

**SYSTEMATIC POSITION**

**PHYLUM:** Chordata

**SUPERCLASS:** Gnathostomata
Fish has a great potential to serve as sensitive indicators, signalling exposure and understanding the toxic mechanisms of stressors in aquatic ecosystems (Mathis and Kevern, 1975). Fish end up being the non target victim of pesticides and other chemicals used in agriculture. Less frequently studied are the implications of interrelated toxic effects on survival, histology, physiology, biochemical constituents and behaviour caused by aquatic pollutants on fish populations. In Barak Valley, tea and paddy cultivation form the major agricultural activities. Needless to say, the shallow water bodies adjoining tea and paddy cultivation practically serve as sink for pesticides, chemicals, fertilizers and some domestic discharges affecting biota in general and fishes in particular. The present study, therefore, investigates the adverse affects of selected heavy metals (Cadmium and Copper) and pesticides (Endosulfan and Malathion) on *Esomus danricus* (Indian flying barb) found in such waters.

1.3 STATEMENT OF THE PROBLEM

Recent years have witnessed significant attention being paid to the problems of environmental contamination by a wide variety of chemical pollutants including heavy metals and pesticides. There is usually considerable concern on the occurrence
of pesticides and heavy metals in the environment due to their persistence and the generally low thresholds of many species. These pollutants build up in the food chain and are responsible for adverse effects and death in the aquatic organisms (Svensson et al., 1994; Farkas et al., 2002). Fish are considered valuable bioindicators at organismic, population, and community levels (Karr, 1981; Wootten, 1990). Among vertebrates, fishes are particularly sensitive to the influence of abiotic factors of the aquatic medium. This sensitivity can be related to their permanent presence in this medium, to their poikilothermy, osmoregulation, nutrition and the ability of aquatic ecosystems to dissolve a great number of natural and synthetic molecules and to transform and/or to concentrate them in various physical and biological compartments. Because of their particular position in the phylogenetic tree and great diversity of their adaptive strategies, fish species share various common physiological features with other higher vertebrates. Because of these reasons, fish not only serve as sensitive indicators of quality of aquatic environments, but also as a useful model to understand by which mechanisms external perturbations may disrupt essential biological functions in other vertebrates. The present study has used a locally available fish species (*Esomus danricus*) as a model system for toxicity studies. *Esomus danricus* is ubiquitous in North India and found in shallow water bodies. In Barak Valley, they are very common in small freshwater systems adjoining paddy and tea cultivation. Pesticides and chemicals used in these crops easily find way to adjoining water bodies and affect the biota in general and fishes in particular. The flying barb is closely related to another Danionin, Zebra fish (*Danio rerio*), which is an important system for biomedical research and numerous molecular and genomic tools are available for their developmental studies. Embryos of *Esomus danricus* are easily maintained in the laboratory using established protocols for Zebra fish rearing and husbandry. Embryos can be obtained year round. Their eggs hatch in two to three days. They are also optically transparent, allowing for fast and easy observations with standard light and epifluorescent microscopy. Information from this study can be used to target further research on developmental effects of anthropogenic contaminants in other fish species. Results obtained in flying barb can be used to develop new indicators of toxicity in other teleosts.
1.4 OBJECTIVES OF THE STUDY

The present study has the following objectives:

1. To estimate Median Lethal Concentrations (LC50) of Cadmium, Copper, Endosulfan and Malathion for *Esomus danricus* (Hamilton-Buchanan) at different time intervals (24-96 hours).

2. To assess the chronic (sublethal) toxicities of the aforesaid metals and pesticides on *Esomus danricus* using various morphological, histological and physiological end-points.

3. To determine MATC (Maximum Acceptable Toxicant Concentration), NOEC (No Observed Effect Concentration) and Acute-to-Chronic Ratios (ACRs) of the metals and pesticides for *Esomus danricus*.

4. To study the uptake, regulation and sequestration patterns of Cadmium and Copper in *Esomus danricus*.

1.5 SCOPE OF THE STUDY

Fish are widely used as biomarkers of environmental pollution to evaluate the health of aquatic ecosystems and their physiological changes (Kock *et al.*, 1996). *Esomus danricus* can serve as an important model for toxicity studies. Information from the present study will be used to target further research on developmental effects of anthropogenic contaminants on other fish species. Besides, biological parameters are sometimes indicative of toxicant effects (Mayer *et al.*, 1992). Therefore studies involving such parameters in flying barb may serve as indicators of toxicants in aquatic systems.
1.6 SIGNIFICANCE OF THE STUDY

The present study estimates Median Lethal Concentrations (LC50) of two heavy metals (Cadmium and Copper) and two pesticides (Endosulfan and Malathion) for a local teleost fish species, the Indian flying barb, *Esomus danricus*. Knowledge regarding acute toxicity study is subsequently used to assess chronic (sublethal) toxicities of the aforesaid metals and pesticides on flying barb using various morphological, histological, physiological and biochemical end-points. Studies on live fishes are abundant but very few are available for this species of fish in India and abroad and especially in North East India. The present study has addressed the impact of selected xenobiotics on this species of fish, which, once abundant in the shallow water bodies of Barak Valley, is fast declining in its natural habitats. Although integration of laboratory data with field situation is beyond the scope of this work, yet in future, an attempt in that direction would definitely be made. Besides, MATC (Maximum Acceptable Toxicant Concentration), NOEC (No Observed Effect Concentration) and Acute-to-Chronic Ratios (ACRs) of the metals and pesticides for *Esomus danricus* have been determined which can enlighten farmers regarding the safe limits of pesticide use in their crop fields. Further, effects of selected essential and nonessential heavy metals and their uptake, regulation and sequestration patterns have been studied and would help in understanding the physiological aspects better. Besides, both Cadmium (discharges from batteries, paints etc) and Copper (use of pesticides like copper sulphate, ‘Paris Green’ etc) also comprise important contaminants in these aquatic systems. Against this backdrop, the present study may be considered to be fairly significant.

1.7 CONCEPTUAL FRAMEWORK

Rationale behind Toxicity tests

The amended Federal Insecticide, fungicide, and Rodenticide Act (FIFRA, 1975) and the Toxic substances Control Act (TSCA, 1976) of USA require risk/benefit analysis based on effects of pollution on Wild biota. The ‘small scale laboratory analysis’
initially consists of acute toxicity tests to estimate the LC$_{50}$ or median lethal concentration of a toxicant. These tests are now called ‘Tier I Tests’ in a multitiered test decision. The LC$_{50}$ tests are statistical estimates of concentrations or doses of a given toxicant necessary to cause death to 50 percent of the test organisms of a ‘representative’ species in a given time frame. Acute LC$_{50}$ tests mostly involve less than 7 days of exposure through food or water. These tests are applied to determine the probability that a toxicant actually influences the test outcome and that differences in effects seen are not due to variations in ‘normal’ populations of organisms (the so called ‘null hypothesis’ or test of ‘no difference’). Extrapolation in a linear manner (derived from the slope of a laboratory LC$_{50}$ suitable from ‘Probit Analysis’ or other dose response curve) to expected or observed environmental concentration is an accepted method for estimating potential ‘hazard’ to representative organisms (Cairns et al., 1978; Finney, 1978; Rand and Petrocelli, 1985). Variables in nature can mitigate or increase toxicity and there are large numbers of species that interact in nature. However, some environmental concentrations of toxicants approaching acute LC$_{50}$ and ‘chronic’ effect levels have been observed to result in similar mortalities in nature (Pimentel, 1971; Brown, 1978). ‘Tier II tests’ in fish consist of 28 day to full life cycle tests if review of Tier I acute tests indicate need for such data. Tier II tests can also be termed as chronic toxicity tests. Problems with chronic toxicity testing with fish are the same as those for acute tests, i.e., mainly in terms of repeatability and standardisation. The possibility for standardisation increases with the understanding of the mechanisms of the observed effects. In Fig.1.7.(i) the “understanding” arrow would also indicate the ‘possibility of standardisation’. Since many of the steps taken to decrease variation in test results, both in intra and inter calibrations, tend to reduce the test, moving it to the right on the “understanding arrow” they also often decrease the possibility to extrapolate results to the environment. The reduction increases the estrangement of the test relative to higher levels of organisations. Some of the endpoints used to measure chronic toxicity are biochemical. The use of these biochemical responses often referred to as biomarkers, to predict potential for adverse effects on survival, growth and reproduction of individuals is based on the belief that a non acute effect
at cellular and organ level can result in an effect on integrated organism functions. Biomarkers may also be defined as a chemically induced change in biochemical systems representing an effect on the systems (Stegeman et al., 1992). Effects of toxicants occur at all levels of biological organisation. Toxic effects are best understood at cell and organ levels where they are also most easily studied, while those at ecosystem and community levels are least understood yet most relevant.

**FIG 1.7.(i): Levels of Toxic effects**

A Maximum Acceptable Toxicant Concentration or MATC is calculated by applying an appropriate factor to an acute effect value, but more precise calculation can be made from chronic effect values. The MATC from chronic effects tests can be calculated from two values: the lowest observed Effect Concentration or LOEC and the no observed effect concentration or NOEC. The geometric mean or MATC is the square root of the product of LOEC times the NOEC (Rand and Petrocelli, 1985; Murty, 1986). In aquatic media, the bio concentration Factor or BCF has been defined as the ratio of substance concentration in an organism to concentration in water (Murty, 1986). Bioaccumulation can be defined as accumulation in a species from all sources (food, water etc.) and biomagnifications can be defined as
concentrations in trophic level representatives. These have been used to 'back calculate' unacceptable concentration in various exposure media (Murty, 1986).

In ecotoxicology, toxicity testing of chemicals is in most cases performed with an intent to extrapolate the results to population, community or ecosystem levels of organisation and predict effects. With these ambitions chronic toxicity tests may, even though they may last longer and require more intensive measurements than acute toxicity tests, still have approximately the same disadvantages in predicting ecosystem effects as acute tests. However, when only population level effects are concerned the tests are often adequate.

Theoretically, any measurable biochemical function of fish can be used as a biomarker. However, using these functions as a measure of stress must be accompanied by knowledge about the importance of the biochemical function on a higher organisational level. Effects revealed with biomarkers are also absolute and can therefore more easily be applied to regulatory decision-making and environmental management (Ewald, 1995). The duration of laboratory exposure requires consideration since different biomarkers show different trends of response over time. Responses also vary with animal, sex, age, nutritional status and season. Internal organs seem to be more indicative of chronic exposures. In a comparative study of several biomarker responses in fish exposed to contaminated sediments, both in the field and in the laboratory, Theodorakis et al., (1992) concluded that the field and laboratory responses were similar, but that the field response was stronger. This could be due to one or more reasons that include species-specific differences between the species used in the laboratory and the indigenous species studied in the field; lifetime toxicant exposure; natural selection; population and community interaction; and abiotic mediating factors in the field.

Histological changes are preceded by biochemical and physiological responses [Fig. 1.7(ii)]. As endpoints, histological changes are not as easily and objectively assessed as the biochemical markers and may require greater experience. But since the damages are not only indicators of exposure to toxic chemicals, but also clear and
indisputable evidence of an adverse effect, test results concluding histological damages at sublethal exposure of chemicals are very difficult to dispute.

**FIG 1.7.(ii): Integration of histopathological biomarkers with physiological and biochemical approaches**

One method of detecting chronic effects in fish is to analyse integrated functions. The integrated functions that are investigated can be divided into two categories: somatic and behavioural. Examples of somatic endpoints are growth rate and scope for growth. Scope for growth is a measure of the energy status of an organism at a particular time. It is based on the concept that energy, in excess of that required for basal maintenance, will be available for the growth and reproduction of the organism.
Composition of a Polluted aquatic Ecosystem

It is well known that various pollutants, including heavy metals and pesticides, are carried to the freshwaters by means of different processes like surface run-off, disposal through wastes, spray drift and direct application. All these methods of translocation of toxicants may occur at a time or may occur individually at different times. Further, the translocation may be by single or multiple means and could cover vast area of land having agricultural fields or forests or wetlands. To boost agricultural production, the forest and semi-arid lands have also been trapped, thereby resulting in immense use of pesticides, which has now turned out to be a source of contamination through surface runoff. From this it can be visualised that there should be progressive addition of pesticides in freshwater ecosystems. The routes of pesticide transport to different aquatic ecosystems have been well documented (Nicholson, 1970). Pollution of an aquatic system occurs by many ways like organic and inorganic chemicals (Doudoroff, 1952; Boetius, 1961; Sastry and Rao, 1981; 1983), oils (Cobioch, 1973), detergents (Schmid and Mann, 1961; Hynes and Roberts, 1962), radioactive elements (Howells and Bath, 1969) and pesticides (Matsumura et al., 1972; Hiltibran, 1974; Chambers and Yarbrough, 1975; Kabeer Ahmmad Sahib and Rao, 1980; Rao and Rao, 1983; Murthy et al., 1983). However, the magnitude of heavy metal and pesticide pollution should be much greater than that of other pollutants, because of the extensive manufacture and applications of these chemical compounds in recent times. Following two heavy metals and pesticides each were considered as test toxicants in the present study:

Cadmium (Cd)

Cadmium is a chemical element with the symbol Cd and atomic number 48. A relatively abundant, soft, bluish-white, transition metal, cadmium is known to cause cancer and occurs with zinc ores. In 2001, China was the top producer of cadmium with almost one-sixth world share closely followed by South Korea and Japan, according to a report by the British Geological Survey.
Cadmium is a ubiquitous, non-essential element which possesses high toxicity to both humans and aquatic organisms. According to Harris and Hohenemser (1978), Cd is classified as the second most dangerous metal in our environment. Its persistence in the environment and rapid uptake and accumulation in the food chain contributes to its potential hazards. Recommended level of cadmium in drinking water is 0.01 μg ml⁻¹ (US and Indian Standards) and 0.005 μg ml⁻¹ according to WHO guideline values. About three-quarters of cadmium are used in batteries, predominantly in rechargeable nickel-cadmium batteries. Besides, Cd is used in electroplating, pigments and plastic production and this has produced sharp increase in contamination of air, water and soil pollution. The European Union banned the use of Cadmium in electronics in 2004 with several exceptions but reduced the allowed content of cadmium in electronics to 0.002 %. Most of the remaining quarter is used mainly for pigments, coatings and plating, and as stabilizers for plastics. Cadmium naturally occurs in the aquatic environment, but is of no known biological use and is considered one of the most toxic metals. Concentrations of cadmium associated with background freshwater systems are estimated to range between 0.05-0.2 μg l⁻¹. While cadmium is also released through natural processes, anthropogenic cadmium emissions have greatly increased its presence in the environment. In aquatic systems, cadmium quickly partitions to sediment, but is readily remobilized through a variety of chemical and biological processes. Toxicity of cadmium to aquatic organisms varies with the type and life stage of organisms, presence of other toxicants and the duration of exposure. Hardness affects cadmium toxicity as well. The toxicity of cadmium increases with increasing temperature (5-20°C) in a freshwater snail species at concentrations of 1-4 mg l⁻¹ Cd. Cadmium can be transported from aquatic to terrestrial food webs by emerging insects. Cadmium removal from aquatic systems by aquatic insects has been shown to be significant: 1.3-3.9 g Cd/year removed by insects out of a total 0.26-19.5 g Cd/year removed. Cadmium concentration is negatively correlated with percent organic matter in natural environments. The presence of zinc and selenium has been shown to antagonize the toxic effects of cadmium. Other metals do not appear to compete with cadmium for receptors in aquatic organisms nor is there evidence for synergistic toxicity. Cadmium poisoning
is an occupational hazard associated with industrial processes such as metal plating and the production of nickel-cadmium batteries, pigments, plastics, and other synthetics. The primary route of exposure in industrial settings is inhalation. Inhalation of cadmium-containing fumes can result initially in metal fume fever but may progress to chemical pneumonitis, pulmonary edema, and death (Hayes, 2001). Cadmium is also a potential environmental hazard. Human exposures to environmental cadmium are primarily the result of the burning of fossil fuels and municipal wastes. However, there have been notable instances of toxicity as the result of long-term exposure to cadmium in contaminated food and water. In the decades following World War II, Japanese mining operations contaminated the Jinzu River with cadmium and traces of other toxic metals. As a consequence, cadmium accumulated in the rice crops growing along the riverbanks downstream of the mines. The local agricultural communities consuming the contaminated rice developed Itai-itai disease and renal abnormalities, including proteinuria and glucosuria (Nogowa et al., 2004). Cadmium is one of the six substances banned by the European Union's Restriction on Hazardous Substances (RoHS) directive, which bans certain hazardous substances in electronics. Cadmium and several cadmium-containing compounds are known carcinogens and can induce many types of cancer. Current research has found that cadmium toxicity may be carried into the body by zinc binding proteins, in particular, proteins that contain zinc finger protein structures. Zinc and cadmium are in the same group on the periodic table, contain the same common oxidation state (+2), and when ionized are almost the same size. Due to these similarities, cadmium can replace zinc in many biological systems, especially systems that contain softer ligands such as sulphur. Cadmium can bind up to ten times more strongly than zinc in certain biological systems, and is extremely difficult to remove. In addition, cadmium can replace magnesium and calcium in certain biological systems, although these replacements are rare. Cd has been shown to inhibit enzyme integrity, interfere with RNA and protein synthesis and to complex with DNA. Tobacco smoking is the most important single source of cadmium exposure in the general population. It has been estimated that about 10% of the cadmium content of a cigarette is inhaled through smoking. The absorption of
cadmium from the lungs is much more effective than that from the gut, and as much as 50% of the cadmium inhaled via cigarette smoke may be absorbed (Friberg, 1983). On average, smokers have 4-5 times higher blood cadmium concentrations and 2-3 times higher kidney cadmium concentrations than non-smokers. Despite the high cadmium content in cigarette smoke, there seems to be little exposure to cadmium from passive smoking. No significant effect on blood cadmium concentrations could be detected in children exposed to environmental tobacco smoke (Jarup et al., 1998).

**Copper (Cu)**

Copper is a chemical element with the symbol Cu and atomic number 29. Copper occurs naturally in the environment and is an essential element for most organisms as a component of some oxidative enzymes. Concentrations of copper associated with background freshwater systems are estimated to range between 0.5-1.0 μg l⁻¹ (Moore and Ramamooorthy, 1984). While copper may form complexes with suspended organic matter, it will ultimately settle out of the water column and be deposited in the sediment. The toxicity of copper to aquatic organisms is dependent on the speciation of the element, water hardness and the type and life stage of the exposed organisms. Total organic content in the aquatic system may decrease copper toxicity, while temperature may also affect copper toxicity, although the relationship is yet to be clearly defined. The distinction between deficiency and toxicity for copper is small for organisms that do not have effective mechanisms to control the absorption of copper (e.g. fungi, algae, and invertebrates).

Copper, though essential in diet can be harmful when large single or daily intake occurs. The harmful effects increase with both the concentration and length of exposure. Copper is a common pollutant in surface waters and its toxicity is largely attributable to its cupric (Cu²⁺) form, which is the species commonly found or readily complexed by inorganic and organic substances and adsorbed onto particulate matter. Complexed copper is biologically unavailable but plants and animals may absorb some copper in the environment. In the unpolluted water, copper may be less than 5
μl l⁻¹ (Alabaster and Lloyd, 1982). Elevated levels of copper may become acutely or chronically toxic to aquatic life. While acute effects may be lethal, chronic effects could lead to reduced growth, shorter lifespan, reproductive problems, reduced fertility and behavioural changes. At low concentrations, copper is an essential element for both plants and animals since it is an important component of enzymes and carries oxygen in crustaceans such as shrimps and lobsters (COPPERINFO, 2001). Higher concentrations of copper have however been introduced into the environment due to anthropogenic activities such as mining, electroplating, paint and pigment industries, textile factory effluents and pesticides. Fish exposed to copper appeared irritable and showed frenzied swimming activity when the bowls were approached. Their bodies were covered with thick mucous. Fish swam upside down and died with mouths opened. These observations were similar to those of Oronsaye and Ogbebo (1995) who worked with adult *Clarias gariepinus* exposed to copper in soft water. Long-term exposure to copper can cause liver and kidney damage and have effects on blood. Studies with animals have shown stomach and developmental abnormalities when excess copper is included in diet (Agency for toxic substance and Disease Registry, 1999). In fish, copper is a classical limiting factor as it is both essential and toxic. As a micronutrient, it is necessary for haemoglobin synthesis and a component of Cytochrome oxidase (Benneth *et al.*, 1995).

**Organochlorine pesticides**

They are persistent pesticides, like DDT, BHC, endosulfan, aldrin, dieldrin, endrin, heptachlor, toxaphene and chlordane etc. Being readily soluble in fats, they accumulate in fat deposits of man and other animals. Rapid elimination of the organochlorine residues in tissues is not possible since they are not metabolised enough in the body (O'Brien, 1967). Hence they are called as ‘hard’ pesticides. These compounds are known to undergo ‘biological magnification (Rudd, 1964; Wilber, 1969; Ranga Rao *et al.*, 1981) and accumulate in ecosystems (Bandy, 1972; Anderson and Defoe, 1980; Guiney and Peterson, 1980; Devi *et al.*, 1981). The blood levels of DDT and its metabolites were found to be higher in Indians than in North Americans (Krishnamurthy and Dikshit, 1982). BHC has been shown to
induce carcinoma in selected species of animals at higher doses. Fish and birds are more susceptible than humans. Lethal concentrations required to bring about such ill-effects can be produced in bird and fish tissues by a single environmental exposure (Krishnamurthy and Dikshit, 1982). Organochlorines are also known to inhibit the ATPase system (Desaiah and Kock, 1975).

**Organophosphorus pesticides**

These are toxic compounds having a phosphorus atom (O’Brien, 1967). The first OP compound synthesized was Tetra ethyl pyrophosphate (TEPP) in 1945 followed by parathion, malathion, and others. That the OP compounds can be used for eradication of pests was first demonstrated by Gerhard and Schrader in Germany (O’Brien, 1967). Presently, there are several OP compounds of different types with different molecular forms like phosphorothioates, phosphorodiathioates and phosphates (Brown, 1978). Some commonly used OPs are malathion, parathion, diazinon, dimethoate, quinolphos, dimecron and penthoate. These pesticides are easily degraded and rapidly excreted. Normally they do not accumulate in tissues. Organophosphates are highly toxic to fishes and are powerful nerve poisons, since they inhibit AChE activity (Casida, 1964; Coppage and Mathews, 1975; Klaverkamp and Hobden, 1980; Lieske et al., 1980; Rath and Misra, 1981). Several workers investigated the toxicity of OP in fish and other animals (Lockhart et al., 1973; Klaverkamp et al., 1977; Johnson and Finley, 1980; Koundinya and Ramamurthi, 1980; Srivasthwa and Singh, 1981; Murthy et al., 1983).

Following are the list of pesticides banned or restricted in use in India:

**Pesticides Banned for manufacture, import and use in India (27)**

1. Aldrin
2. Benzene Hexachloride
3. Calcium Cyanide
4. Chlordane
5. Copper Acetoarsenite
6. Chloromethane
7. Endrin
8. Ethyl Mercury Chloride
9. Ethyl Parathion
10. Heptachlor
11. Menazone
12. Nitrofen
13. Paraquat Dimethyl Sulphate
14. Pentachloro Nitrobenzene
15. Pentachlorophenol
16. Phenyl Mercury Acetate
17. Sodium Methane Arsonate
18. Tetravinphon
19. Toxafen
20. Aldicarb
21. Chlorobenzilate
22. Dieldrine
23. Maleic Hydrazide
24. Ethylene Dibromide
25. TCA (Trichloro acetic acid)
26. Metoxuron
27. Chlorofenvinphos

Pesticide / Pesticide formulations banned for use but their manufacture is allowed for export (2)

1. Nicotin Sulfate
2. Captafol 80% Powder
**Pesticide formulations banned for import, manufacture and use (4)**

1. Methomyl 24% L
2. Methomyl 12.5% L
3. Phosphamidon 85% SL
4. Carbofuron 50% SP

**Pesticides Withdrawn (7)**

1. Dalapon
2. Ferbam
3. Formothion
4. Nickel Chloride
5. Paradichlorobenzene (PDCB)
6. Simazine
7. Warfarin

**Pesticides Restricted for use in India (13)**

1. Aluminium Phosphide
2. DDT
3. Lindane
4. Methyl Bromide
5. Methyl Parathion
6. Sodium Cyanide
7. Methoxy Ethyl Mercuric Chloride (MEMC)
8. Monocrotophos (ban for use on vegetables)
9. Endosulfan
10. Fenitrothion
11. Diazinon
12. Fenthion
13. Dazomet

1.8 CHAPTER DESIGN

The study has been divided into six chapters:

Chapter-I introduces the study. The chapter specifies the objectives, scope, significance of the study and conceptual framework.

Chapter-II goes through an extensive review of literature.

Chapter-III specifies the methodologies involved in the study.

Chapter-IV throws light on the major findings of the study.

Chapter-V goes through extensive discussions of the findings.

Chapter-VI presents the summary of the findings.

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