Chapter 1

INTRODUCTION
The life supporting environmental regime, we call ecosystem, is a very closely interwoven fabric of all living things, coupled with the natural processes, that determine the character, quantity and quality of life that can be supported. Life in the ocean, as life on land, is intimately related to its environment. During the past few decades, human influence on marine ecosystems has been quite significant. Until, man understands the complexities of the aquatic environment so as to fully realize the disadvantageous consequences of his actions, he cannot hope to safely exploit the environment to his advantage. The increasing awareness of the magnitude of environmental problems triggered by human intervention has served to focus attention on the urgent need for sensitive and precise diagnostic tools with a predictive capability for environmental impact assessment.

From oceans life expanded into estuaries, rivers and
lakes. An estuary is "an inlet of the sea reaching into a river valley as far as the upper limit of the tidal rise" (Fairbridge, 1980). Thus, estuaries are highly dynamic systems subject to changes occurring over a spectrum of durations ranging from very short periods to geologic time spans. The flood plain soils of estuaries constitute some of the most valuable agricultural land on earth. Regional seas and near shore areas extending to the edge of the continental shelf often constitute the world's richest fishing zones. Large ports have developed on estuaries or immediately upstream on the navigable rivers that flow into them. Extensive industrial developments are located in these ports and along the shores of estuaries and on the rivers flowing into them. Estuaries are often linked with refineries and oil storage depots, steel and paper mills as well as a diversity of chemical industries (Allan, 1990). In short, the banks of rivers and estuaries became the foci of civilization, because of the favourable features such as the profuse vegetation, fertile soil, access to navigational facilities etc. that have catalyzed the flourishing of human habitats in those regions.

Human association with estuaries and its associated rivers has unfortunately led to their contamination by a variety of pollutants. Public concern for this gross pollution has generated a global demand for initiating regulatory measures to control estuarine and near shore pollution. Pollution has come
to assume such gigantic proportions that it has become virtually impossible to plan its total eradication. A scientific management of the hazard alone seems feasible, if man is to reconcile with the dual imperatives of use and conservation of his planet’s resources. Statutory pollution management guidelines would have to be based on sound scientific advice emerging out of systematic, quantitative and definitive assessment programmes.

GESAMP (1980) have defined aquatic pollution as "the introduction by man, directly or indirectly of substances or energy resulting in such deleterious effects as harm to living resources, hazards to human health, hindrance to aquatic activities including fishing, impairment of quality for use of water and reduction of amenities". Identification of a substance as "hazardous to the environment" involves the determination of its potential for biological damage and the assessment of the chemical’s potential for environmental exposure. The potential biological damage can be evaluated by toxicity tests, both acute and chronic. Acute toxicity tests determine the dose of a particular chemical that will elicit a specific response or measurable end point from a test organism in a relatively short period of time, while chronic toxicity tests investigate the exposure of the organism to a chemical over a prolonged period (van Leeuwen, 1988). Environmental exposure assessment is quantified in terms of its potential
environmental distribution (PED) and potential environmental concentration (PEC), which involve the assessment of environmental fate and transport, identification of exposed populations and environments as well as estimation of expected levels in the environment (Klein et al., 1988).

Of the two hazard evaluation criteria discussed above, toxicity tests have gained wider acceptance in view of their experimental simplicity and have been the subject of several monographs (Philips, 1980; Bayne, 1985; Rand and Petrocelli, 1985). However, its inherent limitations severely restrict the applicability of the laboratory results in predicting the biological impact of the aquatic environment which is distinctly different from that in the laboratory experiments. Environmental exposure assessment, though involving rigorous experimental designs, provides a more realistic assessment of the pollutant's fate in the aquatic environment.

Precise information on the nature of distribution, bioavailability and exchange of trace metals among the different environmental as well as biological compartments of an aquatic ecosystem is essential in evaluating their hazardousness. The present investigation relates to the distribution of trace metals among the different compartments of the Cochin estuary.
The term "trace metal"/"trace element" is used in current literature to designate those elements which occur in small concentrations in natural systems. For all practical purposes, the terms such as "trace metals", "trace inorganics", "heavy metals", "micro elements" and "micro nutrients" are treated as synonymous with the term "trace elements" (Wittmann, 1983). Metals such as Fe, Zn, Cu, Mo, Cr, Co and Mn are essential for life but can be toxic when present at higher levels.

The Cochin estuary has been the subject of several studies, most of which have centered around biological assessment of toxicities of trace metals to estuarine or marine organisms (Lakshmanan, 1982; Sivadasan, 1987; Baby, 1987; Latha Thampuran 1986; Prabhudeva, 1988; Krishnakumar, 1987). Lethal and sublethal effects of trace metal pollutants on biochemical constituents as well as on accumulation and depuration rates have also been documented (Lakshmanan and Nambisan, 1985; 1989; Abraham et al., 1986; Prabhudeva and Menon, 1988; Sathyavanathan et al., 1988; Krishnakumar et al., 1990). Other investigations pertaining to the Cochin estuary relate mainly to studies on nutrients and organic compounds (Sankaranarayanan and Rosamma Stephen, 1978; Murty and Veerayya 1981; Ramani et al., 1981; Venugopal et al., 1982; Paul and Pillai, 1983 a and b; Sankaranarayanan et al., 1986; Lakshmanan et al., 1987; Shibu et al., 1990, Nair et al., 1990, Nair et al., 1991, Ouseph, 1987; 1990).
Scope of the present study

The present study is a marked deviation from conventional toxicity assessments and attempts to initiate investigations in an entirely new perspective - environmental exposure assessment. A pollutant upon release into the aquatic system is carried away from the source by the medium and distributed in due course among the various compartments of the system. A knowledge of the processes that govern the partitioning of the toxicant from the primarily loaded compartment to the adjacent compartments, the factors controlling the equilibria, the sediment-water exchange processes, the inter-compartmental mass transfer rates, etc. define the potential risks of the toxicant to aquatic organisms (van de Meent, 1988).

A scheme of study encompassing all these aspects provides the frame work for the present investigation. Two clams *Villorita cyprinoides* var.*cochinensis* (Hanley) and *Meretrix casta* (Chemnitz) were taken as representative bivalves. Considering the relevance and significance of shells in revealing past environmental history, the bivalves were analysed for trace metal concentrations in soft tissues as well as in shells. Water samples were analysed for trace metal concentrations in both dissolved and particulate phases. Sediment samples were sequentially extracted to separately
analyse the different chemically extractable chemical species present in them. Correlations were struck between various combinations of biological factors and environmental variables. The equilibria existing between the different environmental and biological compartments were evaluated and a mathematical "shell-model" was developed to predict the environmental levels of trace metals from a knowledge of the trace metal concentrations in the shells.

The objectives of the present study were three fold:
(i) to establish the significance of shells in the assessment of aquatic metal pollution levels
(ii) to quantify trace metal bioavailability in terms of the various biological and environmental variables
(iii) to develop a mathematical model for predicting the trace metal concentrations in the various environmental compartments.

In tune with these objectives, the thesis has been divided into six chapters. Chapter 1 gives a general introduction to the subject and highlights the importance of hazard evaluation, risk assessment and management of toxic chemicals and the necessity for environmental monitoring and pollution abatement activities. Earlier reports on the distribution of trace metals in the aquatic biosphere with special reference to the Cochin estuary are also highlighted. Chapter 2 describes the location of the study area. Details of
procedures adopted for sampling, processing and analyses in respect of the investigations carried out in Chapters 3, 4 and 5 are also presented here.

Chapter 3 details the studies carried out on the shells of bivalves with a view to highlighting its significance in environmental stress assessment. Spectroscopic data (IR and EPR) have been used to address the question of influence of mineralogy trace metal enrichment.

Chapter 4 deals with the bioavailability of the trace metals, copper, cadmium, zinc, lead, and nickel to the bivalve *V. cyprinoides var. Cochinensis* (Hanley) which has been assessed in terms of the relationships between the biological factors and the environmental variables (sediment-related as well as water-related). Chapter 5 describes the various equilibria existing between the environmental and the biological compartments of the estuarine ecosystem. The transfer of toxicants from the environmental to the biological system is discussed and a mathematical model has been proposed to aid in the evaluation of environmental stress.

Chapter 6 summarizes the salient results of the present investigation.