Contamination of coastal and estuarine waters by point and non-point pollution sources is a severe water quality problem that has attracted the attention of environmentalists. This interest is based largely on the increased awareness of the presence of contaminants such as trace metals, pesticides and radionuclides as well as of their effects on aquatic ecosystems and their possible toxicological implications to humans.

Acidification of natural waters and trace metal pollution are two important environmental problems facing the world today. Recent investigations on the impact of acid precipitation (acid rain) on aquatic ecosystems have demonstrated that sublethal effects seem to be of greater ecological significance than even large-scale fish kills. An important consequence of acidification is the mobilisation of aluminium from the edaphic to the aquatic environment. These elevated Al levels in acidic waters may be toxic to aquatic biota. The mechanism by which low pH water and combinations of low pH water and elevated Al concentrations become toxic to aquatic organisms are not fully understood. It is the paucity of information on the interactive effects of $H^+$ and $Al^{3+}$ on the bioavailability of trace metals that initiated this study.

Estuaries form a buffer zone between freshwater and the sea. Over the ages, shores of estuaries have been favoured sites for human settlement. Some of the world's highest population densities are found adjacent to major estuarine systems. Estuaries have been used as convenient conduits for the disposal of a broad spectrum of wastes generated by industries and for sewage disposal. As a consequence of these activities, estuaries in industrialised nations commonly are highly stressed environments. Trace metals constitute a serious threat to the stability of the estuarine
ecosystem. An appreciation of the role that these substances play on the health of an estuary requires a thorough understanding of their chemical, physical and biological dynamics in the system.

The objectives and scope of the present study along with the considerations for the selection of the metals Cu, Cd, Hg and Al are detailed in Chapter I. The suitability of Villorita cyprinoides var cochinensis as the bioindicator is also discussed.

The different experimental designs employed for both acute and sublethal studies and the methods for the determination of filtration rate, metabolic rate, bioaccumulation and depuration of trace metals and various biochemical constituents (glycogen, lactic acid, lipid, protein and ascorbic acid) are given in Chapter II.

The location of the sampling sites in the Cochin estuary, the speciation scheme used for the determination of different forms of Al and of the methods of determination of hydrographical parameters and Al are presented in Chapter III.

The temporal and spatial variations of various hydrographical parameters like salinity, pH, DOC, POC, DO along with the different forms of Al in the Cochin estuary were measured. The correlations of Al fractions to different hydrographical parameters were dependent on seasons and the correlations varied with sampling periods. Particulate aluminium, total dissolved aluminium, total monomeric aluminium and filterable cation exchange aluminium were found to be negatively correlated to pH, salinity and suspended matter whereas, these forms were positively correlated to particulate organic carbon. The correlation between dissolved organic carbon and different fractions of Al varied with season. Labile aluminium and colloidal aluminium fractions were negatively correlated to suspended matter whereas they were positively correlated to dissolved organic carbon during post-monsoon. Labile and colloidal aluminium were found to be uncorrelated to salinity or particulate organic carbon. All fractions of Al were positively
correlated to dissolved oxygen during all seasons. There was no well-defined relationship between the temperature and Al in this estuary.

The maximum value of total dissolved aluminium (63.15 μg l⁻¹) was observed in freshwater zone during monsoon and the minimum value (2.32 μg l⁻¹) was found in the marine region during pre-monsoon. The maximum value of Al observed in the riverine region may be due to the acidification processes occurring in the upper reaches of the river Periyar; the minimum value could be attributed to the active removal mechanisms present in this estuary. Salinity, pH, adsorption, sedimentation, dilution and biological processes are responsible for the removal of Al in this estuary. Because of these active removal mechanisms, Cochin estuary acts as a sink for Al. The marked correlation values between salinity and total dissolved Al and the marked departure from the dilution line suggest that Al behaves non-conservatively in this estuary. Therefore, the input of this estuary to the contribution of Al in the Arabian sea is very little.

Trace metal toxicities and the interactive effects of H⁺ and Al³⁺ on the physiological parameters like filtration rate and metabolic rate have been described in Chapter IV. The interactive effects of H⁺ on the trace metal toxicities varied and depended on the chemical speciation and on the nature of biological systems. The presence of Al³⁺ increased the toxicities of Cu, Cd and Hg. This may be due to the change in bioavailability of the trace metals in presence of Al as well as to the toxic effect of Al³⁺. The toxicities of the trace metals used in this study varied (based on LC50 values) in the following sequence:

Hg > Cu > Cd > Al

Reduction of pH modified the toxic effects of Cu and Cd in a largely protective fashion whereas in the case of Hg the toxicity increased.
Filtration and metabolic rates of the clam were found to be suppressed by trace metals at different pH. The variations could be explained on the basis of production of mucus during the exposure of the clam to different metals at different pH, bioavailability of metals at the gill surface and interactions of $H^+$ and trace metals with the physiological characteristics like valve-movement and cell-morphology.

The accumulation of trace metals at different pH, the depuration of accumulated metals at pH 7.6 and the interactive effect of $Al^{3+}$ on the bioavailability of Cu, Cd and Hg have been discussed in Chapter V. The accumulation and depuration were found to be linear and the bioavailability was found to be dependent on pH. This may be due to the changes in chemical speciation of metals and competitive interaction of $H^+$. The changes in physiological parameters like filtration rate and metabolic rate and the changes in the adsorptive ability at the biological surface also appear to have contributed to the variation in accumulation and depuration of trace metals. By comparing BCF (bioconcentration factor) values after 120h of Cu, Cd, Hg and Al, the order of their accumulation in the soft tissues of the test specimen was found to be

$$Hg > Cu > Cd > Al$$

which is in very good agreement with the order of toxicities based on LC50 values.

The depuration of trace metals accumulated at different experimental conditions was compared using biological half life periods ($B_{1/2}$). $B_{1/2}$ values of Cu, Cd, Hg and Al were measured and on their basis these metals could be categorised into two of the three groups suggested by Cunningham and Tripp (1975b). Group I consists of Cd in which $B_{1/2}$ increased with increase in body burden of the metal and Group II consists of Cu and Al where $B_{1/2}$ decreased with increasing body burden of trace metal. Depuration of mercury was found to be a complex one and Hg belonged to Group I.
during low body burden and changed to Group II with increase in the initial concentrations of Hg.

In general, the variations in the accumulation and depuration of Cu, Cd, Hg and Al at different pH and the interactive effect of Al$^{3+}$ could be explained based on the competitive interaction of H$^+$ for binding sites, the metal chemistry, the enhanced and varied mucus secretion, the variation in the speciation of metals, the several detoxification mechanisms, the alterations in metabolic processes such as metabolic rate and filtration rate as well as other biochemical changes.

Biochemical responses to trace metals have been acknowledged as reliable indices for environmental monitoring purposes. Biochemical constituents like glycogen, lactic acid, lipid, protein and ascorbic acid in the test specimens exposed to sublethal levels of trace metals at different pH were measured. Depletion was observed in the glycogen, lipid, protein and ascorbic acid contents of the clam whereas, an elevation was noticed in lactic acid content. These variations were found to change with pH. The results of this investigation have corroborated the relevance of glycogen, lactic acid, lipid and protein contents as useful indices of stress even in the context of competitive interaction between H$^+$ and Al$^{3+}$ ions. Ascorbic acid content however, was not found to be very good index for predicting the trace metal stress.

Considering the magnitude of the environmental acidification problem and the complexities of pH-Al synergism, it is abundantly clear that a holistic appreciation of a particular environmental regime would be possible only after further and detailed investigations on the mechanisms of accumulation at the molecular level are carried out.