CHAPTER 2

Scope and Summary of the Work

Heavy metal flux to the NE coast of Bay of Bengal from Hooghly river, the first deltaic offshoot of the river Ganges seems to be considerably increased due to the growing industrialisation and urbanisation along the bank of the river. Sundarban mangrove forest is situated at the estuarine phase of Hooghly river which exhibit large property gradients in the mixing zone of the river and can be regarded as acting as filters of river transported trace metal.

The land-ocean boundary condition in the Sundarban, NE coast of Bay of Bengal is highly irregular and criss-crossed by several creeks and water ways. There are about 54 islands covered with thick mangrove forests. High litter production from the forest subecosystem along with *in situ* high biological occurrence in the aquatic subecosystem results in the high production of humic substances which are resistant to biological degradation both in the water and in the sediment. The humic substances constitute the predominant form of organic matter present in sea water and soils. This humic substances may form complexes with the toxic metals, lowering the toxicity of the metals and also on biota. Studies on complexation of humic substances with trace metals and their effects on bioavailability and toxicity to biota in Sundarban mangrove system are very important in understanding the fate of those toxic metals in this enviornment. No information is available on the complexation study of humic substances with trace metals in this estuarine system. The present work is intended to fill this gap and to present a comprehensive picture about the nature of complexation of humic substances with trace metals, their effects on bioavailability and toxicity to biota and finally the fate of the toxic trace metals.

Humic (HA) and fulvic acids (FA) were extracted and elemental and chemical characteristics of humic and fulvic acids were also performed.

pK_A values for HA and FA and formation constants of the complexes with metals like Fe(III), Cu(II), Zn(II) and Co(II) were determined by potentiometric titration .

Spectral characteristics of humic and fulvic acids were determined using Infra-red, UV-VIS and fluorescence spectroscopy.

A non-electrochemical approach, Synchronous fluorescence spectroscopy was also explored for the determination of the stability constant. The adsorption of Cu(II), Zn(II) and Co(II) onto the different sediments were studied at different temperatures and salinities at pH 4.5. Using the principle of adsorption isotherm, values of partition coefficient (K_d) for different metals at different salinities were determined.

Adsorption of metals on different phases, FeO_x phase and organic phase (HA & FA) in the sediment were also critically examined. Linearised Langmuir isotherm equation was applied to determine the adsorption coefficient (K). The kinetic study for the adsorption of metals on the sediment showed the first-order nature from where values of adsorption (K_1) and desorption coefficients (K_2) were determined.

Trace metal concentrations (Fe, Co, Cu, Zn) in the tissue of *M. birmanica* occurring in the Sundarban mangrove environment were studied and their accumulation in the bivalve was found in the same order as they are found to occur in the sediment. But the enrichment of Zn was considerably higher in comparison to the other metals indicating that Zn was more loosely bound at the binding sites of HA and FA occurring in the sediment. A detailed biochemical study in relation to Zn accumulation in *M. birmanica* was performed. Monthly variations of glycogen content per individual and seasonal variations of concentration of Zn in *M. birmanica* was found species specific and it could be used as bioindicator for Zn-contamination.

In chapter 1, an introduction including a literature survey of research on different international and national seas are coverd. The objectives of the present study and its importance is also discussed.

Chapter 2, deals with the scope and summary of the work.

Chapter 3, deals with the description of the study area of Sundarbans, India. Four stations are selected to collect water and sediment samples and only one station is selected to collect the *M. birmanica* specimens.

Chapter 4, covers the theory and experimental procedure for the work. The chapter also covers the methodology of the work. Extraction procedure for humic substances, experimental setup for potentiometric titration and synchronous fluorescence spectroscopic method are discussed in detail. Estimation of fulvic and humic acids in the sediment, trace metals in the biomass and sediments, collection of specimen and the measurement of their metabolic rate, organic carbon determination, dissolved oxygen in water, nitrate-nitrogen, phosphate-phosphorus, salinity, estimation of protein, carbohydrate, silicate-silicon in humic substances are discussed in detail.

Chapter 5 covers the results and discussion of the work. In the subsection 5.1 sediment characteristics are discussed in detail. The subsection 5.2 covers the analytical characteristics of humic and fulvic acids. Spectral characteristics of humic substances are discussed in the subsection 5.3. Complexation study of humic and fulvic acids with metals by potentiometric and fluorescence method are discussed in subsection 5.4. Adsorption of metals onto the oxide phase of iron and organic phase are discussed in the subsection, adsorption isotherm 5.5, from where partition coefficient (K_d), adsorptoin maxima (Γ_m), adsorption coefficient (K) and kinetics of adsorption are determined. Subsection 5.6 deals with river run-off of metal from where flux of metals are calculated. In the subsection 5.7 biochemical studies in relation to Zn-accumulation in the species *M. birmanica* are discussed and in the subsection 5.8 seasonal variation of concentration of Zn in *M. birmanica* shows its species specific nature and it can be used as bioindicator for Zn-contamination.

Chapter 6, summarise the results presented in the preceeding chapters with comprehensive discussion of all constituents in relation to humic substances, their complexation with trace metals and their effects on bioavailability and toxicity to biota.