CHAPTER 6

Conclusion of the work

Fluxes of some metals viz. Cu, Zn Fe and Co from the Hooghly estuary to the Sundarban mangrove environment, NE coast of Bay of Bengal were found to be 5.6, 6.97, 5250 and 2.493 μg cm^{-2} yr^{-1}, respectively. Sediment in the mangrove environment was found to act as a sink for these metal and their *in situ* concentrations were found to be several fold lower in magnitude than the maximum adsorption concentration. In order to find out the possibility of the sediment to act as a sink for heavy metal, attempt was made to characterize the binding of metal with humic substances (Fulvic acid and Humic acid) and oxide phase occurring in the sediment. The annual production of humic substances was found to be 0.106 g cm^{-2} yr^{-1}. Fulvic acids the major component of humic substances were found to be about 2.4 to 3.4 times higher than those of humic acids in the mangrove sediment.

IR spectra of HA and FA showed the presence of –OH, -COOH groups and exhibited their aromatic nature. The specific UV-absorption was higher for HA compared to FA which could be explained by a core with higher aromaticity in the case of HA.

Fluorescence study showed that both HA and FA were highly fluorescent compounds. Conversion of fulvic acid (FA) to humic acid (HA) resulted in the red shift of the emission maxima with reduced intensity of fluorescence, indicating aromatic condensation with inclusion of more –COOH groups. It was noted that humification resulted in the decrease of acid strength at the ligand sites and in the excited state these acidic groups had different acidic strength. Ligand sites of humic substances were characterized by quenching of SyF bands with different metals, differing with respect to their functional group affinity. The increase of loosely coupled electron withdrawing (-COOH) substituents to the rigid framework (aromatic structure) results in the reduction of fluorescence intensity due the depletion of vibronic energy through these substituents. The process has been found to be enhanced through the formation of σ-bond with metal. Lower values of

log K_c (conditional stability constant) were obtained by potentiometric method at pH 5 than those obtained by fluorescence method at pH 7, indicating increased stability of the complexes at neutral pH and more stable complexes were formed by FA in comparison with HA. Again Fe(III) formed most stable complexes with both FA and HA than Cu(II), Zn(II) and Co(II) at both pH 5 and 7. The values of conditional stability constants on the Iron-oxide phase indicating the formation of ternary surface complex with humic acid and the order of stability was found to be Cu> Zn> Co. Adsorption of Cu, Zn and Co onto the sediments at different temperature and salinity followed the Langmuir type of adsorption process and indicated chemical interactions at the adsorption sites. This substantiated the formation of ternary surface complexes. The kinetic studies for adsorption of metals at a constant temperature and constant salinity with respect to the sediment supported the first order adsorption phenomena.

Bioavailability of metals with respect to their accumulation in the bivalve (*M. birmanica*) was found in the same order (Fe> Zn> >Cu >Co) as they were found to occur in the sediment . But the enrichment factor of Zn was high with respect to both SPM and surface sediment. It was concluded that both Fe and Zn were strongly bound at the binding sites of HA and FA occurring in the sediment at *in situ* pH, which seemed to have considerable role for their increased bioavailability. The complex interactions between food availability, reproductive activities and accumulation of Zn were observed during the development and seasonal metabolic cycle of the bivalve. Metabolism of protein and glycogen took place during initial stage of the breeding time (pre-monsoon) and their concentration attained minimum value during monsoon time. Increased concentration of tissue zinc, resulted anaerobiosis and minimum value of the ratio of respiration to ammonia excretion (O/N) was obtained. Higher value of (O/N) ratio were observed during post and pre-monsoon under increasing supply of food and low concentration of zinc. Glycogen stored during pre-monsoon followed

anaerobic metabolic path to oxaloacetate induced by high zinc concentration in the tissue at low salinity (monsoon). Thus seasonal variation of concentration of Zn in *M.birmanica* was species specific and it could be used as bioindicator for zinc contamination .