

**COMPARATIVE STUDY OF COPPER CONTAMINATION  
IN THE WATER AND SEDIMENT COLUMN OF THE  
RAMNA LAKE AND DHANMONDI LAKE**

BY  
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A thesis submitted to the Department of Civil Engineering of Bangladesh University of Engineering and Technology, Dhaka in partial fulfillment of the requirements for the degree

of

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## DECLARATION

I hereby certify that the research work embodied in this thesis has been performed by the author under the supervision of Dr. A.B.M. Badruzzaman, Associate Professor of the Department of Civil Engineering, BUET. Neither this thesis nor any part of it has been submitted or is being concurrently submitted else where for any other purpose (except for publication).

January, 1998

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Hafiz Ahmad

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## ABSTRACT

The primary objective of this study was to assess the level of copper contamination in the lake water and sediment of Dhanmondi and Ramna lakes. The other major objectives were determination of equilibrium speciation of copper in lake water in order to assess its toxic effects, determination of spatial distribution of major copper species, evaluation of copper adsorption characteristics on different sizes of bed sediment particles of both the lakes and assessment of gross bioaccumulation of copper in fish.

Water and sediment samples of Dhanmondi and Ramna lake were collected from different sampling locations for laboratory analysis during three different periods of the year namely, dry period (April to May), wet period (June-July) and intermediate period (August-January). Sediment samples were collected to assess the nature of copper adsorption on the bed sediment particles. In addition, bioaccumulation of copper in fish of the lake was assessed by determining copper concentrations in various parts including gill, stomach etc. of a fish (*Nilotica*) of Dhanmondi lake.

Both the Dhanmondi and Ramna lake water and sediment layer were found to be heavily contaminated with copper. Maximum and minimum concentration of copper in the water of Dhanmondi lake was 0.2913 mg/l and 0.062 mg/l and in Ramna lake 0.2047 mg/l and 0.0723 mg/l respectively. Major aqueous copper species found in both the Dhanmondi and Ramna lakes were  $\text{Cu}(\text{OH})_2$ ,  $\text{Cu}^{2+}$ ,  $\text{CuCO}_3$ , concentration of  $\text{Cu}(\text{OH})_2$  was maximum.  $\text{Cu}^{2+}$ , the free and most toxic form of copper species was also present in considerable amounts. pH was found to be the major controlling factor for copper speciation. With a decrease in pH, ionic copper ( $\text{Cu}^{2+}$ ) concentration increases thus increasing the toxicity of water. Conversely, with an increase in pH, ionic copper concentration decreases with increased adsorption reducing toxicity.

Analysis of sediment samples suggest that maximum amount of copper was adsorbed on particles retained on sieve #30, #40, #50 (i.e. size < 1.19mm. to > 0.297mm.). In most

cases copper absorption increased with the decrease in particle size upto a certain level (0.42 mm). After that particular particle size, copper absorption decreased with the decrease in particle size. From the analysis of bed sediment it was found that maximum copper concentration in top and bottom layer of Dhanmondi lake was 59.45 mg/kg and 52.28 mg/kg respectively. In Ramna lake copper concentration in top and bottom layer was 47.77 mg/kg and 46.21 mg/kg respectively.

Study of bioaccumulation of copper revealed that copper is present in excessive amount in the different parts of fish in Dhanmondi lake. Maximum copper concentration was found in the stomach (7.442 mg/kg) of fish. Thus, human consumption of the fishes from Dhanmondi lake may be harmful.

At present renovation work is underway at the Dhanmondi lake. It seems that the lake is being dredged indiscriminately and the dredged spoils are being piled along the shore. If not done upto a proper depth this dredging process is likely to expose the heavily contaminated deeper sediment layer to lake water. The freshly filled lake water will get contaminated with copper through diffusion and desorption from the newly exposed bed. In addition, the dredged spoils piled along the shore may release copper following rainfall into the lake and surrounding areas.

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## CHAPTER - 1 INTRODUCTION



### 1.1 GENERAL

Contaminants including trace metals and toxins in water and sediments constantly impose threat to aquatic species as well as humans. Distribution of toxic trace metals and other materials among water systems and sediment of lakes and reservoirs is a common problem which causes hazard associated with pollution of aquatic system. Use of a water body such as lakes and reservoirs as an urban disposal site could cause unnaturally high concentrations of such pollutants in water column as well as in sediment. In recent years, studies on contamination, speciation of heavy metals in lakes and reservoirs and their removal are being conducted all over the world show that heavy metal contamination is more likely to occur in urban / industrial areas. Ramna and Dhanmondi lakes - both are situated at the heart of Dhaka city, one of the most densely populated cities in the world. Of these two lakes, Dhanmondi lake has been receiving industrial as well as domestic sewage for a long period of time. So, it is likely to be heavily contaminated with heavy metals. On the other hand, Ramna lake receives reduced pollutant load, since there is no major waste inlet. A comparative study on heavy metal contamination of these lakes may be conducted to see the effect of variable domestic and industrial waste input.

Copper is a common heavy metal and is toxic to both human and aquatic lives, even in trace amount. It is considered as a probable carcinogen, which may cause brain and kidney damages. It imposes threat by resulting accumulation in the food chain and their potential health hazard in drinking water supplies (Moore and Ramamoorthy, 1984). As both of these lakes receive effluents from different drains regularly, they are likely to be contaminated with copper. Such non-flowing lakes, once contaminated with heavy metals like copper have little chance of purifying naturally. Copper is gradually absorbed on to suspended solids of lake water and settles quickly causing accumulation in the sediment bed. Sediment water interaction causes the pollutant to persist longer in the aquatic

environment, which in fact pose a great threat to water quality. Since adsorption of copper on sediment depend on the surface area available for adsorption, size of the particle also influence on the quality of water.

Ramna lake is generally used throughout the day for bathing purposes by low income group. Dhanmondi lake is primarily used for recreational purpose. It is a popular fishing spot for amateur anglers. Bangladesh Fisheries Department, management authority of the Dhanmondi lake, earns a lot of money through pisciculture in this lake and also through leasing to Bangladesh Amateur Anglers Association who in turn sell tickets to interested persons for angling. So it is important to investigate the water quality like copper contamination in these two lakes.

Copper may be present in ionic form or as soluble complexes or in sorbed state in an aquatic system. Toxicity of copper depends on the chemical form in which it exists in a system. Determination of the concentration of the pollutant (copper) in the water body and in the system is not enough, copper speciation (determination of chemical forms of any constituent under equilibrium condition is equilibrium speciation) is an urgent necessity. Chemical speciation of trace metal is also influenced by physico-chemical factor (pH, temperature, complexing agent). In addition, sorption of copper depends on the availability and the nature of the sorptive surface. Thus, grain size distribution of the bed sediment may provide information on the adsorption of copper.

## **1.2 OBJECTIVES**

The primary objectives of the study are:

- To compare the status of copper pollution by determining its concentration distribution at different locations and at different time periods of the Ramna and Dhanmondi lakes and thereby assessing impact of sewage disposal on copper pollution of aquatic system.

- To determine the equilibrium speciation of copper in Ramna and Dhanmondi lakes under different physical conditions (pH and temperature ).
- To identify any possible relationship between grain size of bed sediment and the adsorption of copper.
- To assess the concentration variation of copper species during wet and dry periods in both lakes.
- To assess gross bio-accumulation of copper in fish in Dhanmondi lake.

### **1.3 SCOPE OF THE STUDY**

Ramna lake and Dhanmondi lake - both are situated at the heart of Dhaka city. A number of domestic sewage inlets and urban runoff enter into these lakes. Knowledge of distribution of copper in different forms in the lake water as well as in bed sediment is essential in determining the toxicity level of the system. Persistence as well as transport of metal in a system depends on the total concentration and chemical form of metal. Thus high level of copper in different form may make aquatic inhabitants toxic to human consumption. In this study, a comparative study of chemical speciation of copper (which refers to the tendency for a compound element to assume a variety of aqueous forms in response to environmental factors such as pH, temperature, and the interaction with organic and inorganic copper compound in Ramna and Dhanmondi lakes) has been performed.

Copper may be present in ionic form or as soluble complexes or in sorbed state in an aquatic system. Toxicity of copper depends on the chemical form in which it exists in the system. So determination of the concentration of these pollutants in the water body and in the system is not enough. That is why copper speciation is of great importance. Since a comparative study of copper speciation in water and sediment of Ramna and Dhanmondi lakes have not been conducted yet, it is a timely and appropriate approach to study the



fate of copper in the aquatic environment. Heavy metals like copper adsorbed with suspended solids of lake water settle quickly and accumulate on the sediments. The sediment water interaction causes the pollutant to persist longer. Through this research, sediment water interaction on metal concentration in water column can be quantified. The necessity for applying environmental regulation on these two lakes on priority basis may be suggested through this work .

Bangladesh Parjatan Corporation and Dhaka City Corporation have plans to convert the lakes into tourist resorts with development of fishery facilities and building of floating restaurants. This study may provide information on the possible options in restoration of these lakes with minimal adverse effects on the surrounding environment and human lives.

#### **1.4 ORGANIZATION OF THE THESIS**

The thesis consists of five chapters. Apart from this chapter, the remainder of the thesis has been divided into another four chapters.

Chapter 2 includes literature review covering impacts of heavy metals, especially copper. This chapter emphasized on sources, speciation, transport and distribution of copper in aquatic system. Brief description of copper chemistry and number of reviews of relevant literature are also discussed in this chapter.

Chapter 3 consists of brief description of the methodology applied in the work. Sampling locations of the lakes, sampling program, collection, preservation and storage, and analysis of water and sediment samples as well as fish sample are described in this chapter.

Chapter 4 presents an evaluation of copper contamination in Dhanmondi and Ramna lake based on the laboratory analysis of water and sediment samples collected from the lake. Spatial and seasonal variation of copper and other relevant chemical constituent are

discussed. This chapter mainly presents results of equilibrium speciation calculations performed by using MINEQL<sup>+</sup> (Schecher,1994). Major aqueous copper species have been identified and their relative toxicities are discussed here. Effect of various parameters (e.g. pH) on speciation and resulting variation in toxicity are described. Relationship between grain size of bed sediment and the adsorption of copper is assessed. Adsorption of copper on top and bottom sediment layers was also determined. This chapter also presents results on bioaccumulation of copper in various tissues of fish species of Dhanmondi lake. Level of contamination and its implications are also presented in this chapter.

Finally Chapter 5 presents major conclusion of the study and also provides recommendation of future study.



## CHAPTER -2

### THEORY OF COPPER CHEMISTRY

#### 2.1 COPPER IN AQUATIC SYSTEM

In aquatic environment, copper exists in three broad categories: particulate, colloidal and soluble. The dissolved phase could contain both the free ion as well as copper complexed to organic and inorganic ligands.

##### 2.1.1 Copper Transportation in Natural Waters

Particulates contain varying fractions (12-97%) of total copper transported by rivers. Approximately  $6.3 \times 10^6$  metric tons of copper are transported annually by rivers to the oceans. Only 1% of this is in the soluble form, 85% in particulate crystalline phases, about 6% bound to metal hydroxide coating, 4.5% bound to organic and only 3.5% adsorbed into the suspended solids. (Moore and Ramamoorthy, 1984)

From size fraction studies of the Ottawa River water, Ramamoorthy and Kushner(1975) showed that about 35% of added  $\text{Cu}^{2+}$  was bound to suspended solids( $>0.45 \mu\text{m}$ ) and 48% to macromolecules( $\leq 0.45 \mu\text{m}$ -45000 MW fraction). The rest was bound to size fraction less than 1400 MW. The binding components were identified to be organic compounds. Similarly 40-60% of total copper in estuarine and coastal waters was associated with colloidal matter of organic and inorganic forms.(Batly and Gardner, 1978)

From an eight years' study (1970-78) on the transport and budget of heavy metals in the Ruhr river, Inhoff et al(1980) reported that (i) copper showed a small range of variation in concentration even with changing flows (ii) the extent of variation was independent of the sampling stations along the river. The relatively small variation in levels was

attributed to the equal input from geo-chemical origin of non-point sources. About 65-81% of copper was in the soluble fraction, thus minimizing concentration fluctuations.

### **2.1.2 Copper in Fish**

Residues in marine fish are generally higher than those in fresh water species. In polluted fresh waters, maximum concentration of copper in muscle tissue seldom exceed 1 mg/kg wet weight. Fish collected from polluted marine waters generally contain 0.5 - 2.0 mg/kg in muscle tissue, extreme levels of environmental contamination may lead to muscle concentrations of 3 - 6 mg/kg. Because muscle residues are generally low, copper does not pose a threat to most fisheries, even those in polluted waters.

Roth and Hornung (1977) reported that total copper in water, sediment, and algae from the Mediterranean coast of Israil averaged 3.7  $\mu\text{g/l}$ , 1.6 mg/kg, and 5.4 mg/kg dry weight, respectively. Residues in the 12 most common fish were 3.8 mg/kg dry weight, yielding CF's of 1000 and 2.4 based on water and sediment as the polluting source, respectively.

Residues in the liver of Eel, Whiting and Flounder from the Medway Estuary (UK) were 5-60 times greater than those in muscle (Wharfe and Van den Broek, 1977). This was also noted for Roach and Crucian Crap in central Europe (Drbal, 1976) and Flounder from Baltic sea (Von Westernhagen et al, 1981). Although the gut-wall is another major site of deposition, concentrations in skin and gills are approximately similar to those in muscle. In some species, ovaries accumulate substantially more copper than testes.

Contaminated food is probably a more important source of copper than water. So burdens in fish cannot be consistently related to ambient pollution levels in water. Rate of uptake is inversely related to the presence of chelators and inorganic ions in the water, and directly related to the exposure period and concentration. Although residues in muscle tissue frequently decline with age and size of the fish, McFarlane and Franzin (1980) demonstrated a consistent positive correlation between copper in pike livers and fish age.

This implies liver analysis provides a better analysis of the health of fish populations than muscle analysis.

### **2.1.3 Copper in Sediment**

Copper is sorbed rapidly to sediment, resulting in high residue levels. Rate of sorption varies with the type of clay/sediment, pH, the presence of ligands and Fe/Mn oxides.

In the lake Ontario, all of the copper in sediment was bound to humic acid (Nriagu & Coker, 1980). Tessier et al (1980), from studies of Yamaska and St. Francois Rivers (Canada), reported a high percentage of organic bound copper in the particulates. The fractions from the two rivers were: organic 31% and 52%, residual 41 and 22%, Fe-Mn oxides 20 and 12%, carbonate 8 and 14% and exchangeable 1.0 and 1.2%. These values were different from Amazon and Yukon Rivers where organic-Cu was 8-15% and residual fraction 74-84% (Gibbs, 1977). Similarly Willey and Fitzgerald (1980) reported that about 27% of organic bound-Cu occurred in coarse sediment ( $\geq 63\mu\text{m}$ ) and 62% in the fractions.

Desorption from sediment into the bulkwater depend on pH, salinity and the presence of natural or synthetic chelating agents. Van der Weijden et al. (1977) reported the order for decreasing desorption into 1:1 diluted seawater and encounter to be  $\text{Cd} > \text{Zn} > \text{Mn} > \text{Ni} > \text{Co} > \text{Cu} > \text{Cr}$ . No desorption of Fe and Pb was reported. Elevated copper levels ( $\geq 1000$  mg/kg dry wt.) in sediment are often associated with the discharge of mine waste. Although other industrial sources may produce residues of upto 500 mg/kg, concentrations associated with sewage disposal are generally  $\leq 250$  mg/kg. Unpolluted marine freshwater sediments generally contain levels  $\leq 20$  mg/kg.

### **2.1.4 Residues of Copper in Water and Sediment**

Soluble copper level in uncontaminated fresh water unusually range from 0.5 to 1.0  $\mu\text{g/l}$  increasing to  $\geq 2\mu\text{g/l}$  in urban areas. Much higher concentration (500-2000  $\mu\text{g/l}$ ) occurs

in vicinity of some metal mines and during the periods of high water (Tyler and Buckley, 1973). There is a gradual decrease in residues moving from coastal marine waters to off shore areas. Duinker and Nolting (1977) showed that soluble copper exceeded 15  $\mu\text{g/l}$  in the Rhine Estuary, but decreased to  $\leq 0.2 \mu\text{g/l}$  in the English Channel. Similarly, concentration of 1-5  $\mu\text{g/l}$  have been reported for the Mediterranean and Baltic Seas, a reflection of elevated anthropogenic loading, whereas open oceanic waters have residues of  $\leq 2 \mu\text{g/l}$ .

### 2.1.5 Copper in Aquatic Plants

Concentration in attached species inhabiting polluted waters generally average 10-100 mg/kg dry weight. Residues in *Ascophyllum nodosum* collected from a polluted part of Trondheimsfjord (Norway) averaged 166 mg/kg whereas in a controlled area they contained 6 mg/kg (Haug et al. 1974). A mixed population of benthic algae had copper level of 120-335 mg/kg throughout a 150 km section of Neckar River (FRG) ( Bartelt and Frostner, 1977). Trollope and Evans (1976) reported levels of 660 mg/kg in unattached filamentous species inhabiting a Welsh fish near a smelter and 140 mg/kg in a control area.

CF's for copper are lower than those reported for most other heavy metals, including mercury, Cd, Pb, Zn, Ni. Depending on the extent of ambient pollution. CF's may range from  $0.1 \times 10^3$  to  $\geq 1 \times 10^5$  in both marine and fresh waters. In Ruhr river (FRG), average CF's for *Nupher Inteum* (Spermatophyta) and *Hygroamblystegium* species (Bryophyta) were 78 and 2800, respectively (Dietz, 1973). Rate of uptake depends on the initial concentration of Cu in the media. Although appreciation sorption occurs in the presence of  $\text{Na}^+$  and  $\text{Mg}^{2+}$ , uptake is generally suppressed by  $\text{H}^+$ . Sorption rates are species dependent resulting in variable residues levels among different species. Further more Cu may increase the permeability of the cell wall in aquatic plants, thereby increasing susceptibility to other pollutants.



### 2.1.6 Copper in Invertebrates

Invertebrates inhabiting polluted freshwater generally carry residues of 5-200 mg/kg dry-wt. in soft tissue. Manly and George (1977) reported levels of 21-103 mg/kg in the mussel *Anodonta anatina* found in the river Thames (UK). Similarly, concentration in herbivorous, omnivorous invertebrates collected from a stream in an industrial area of USA (Wisconsin) averaged 13.7, 70.9 and 30.5 mg/kg, respectively (Anderson, 1977). Copper sulfate was added to an irrigation canal in California (USA) to control algae, resulting in water, sediment and vascular residues of  $\leq 0.01$  mg/kg, 30-60 mg/kg and 35 mg/kg dry-wt., respectively (Fuller and Averett, 1975).

Residues in marine invertebrates are often much higher than those reported for fresh water. Some of the highest residues for marine invertebrates have been reported for the Bristol Channel and Severn Estuary (UK). Stenner and Nickless (1974) reported maximum levels of 1750 mg/kg by weight for soft tissues of molluscs *Nucella lapillus*, whereas the oyster *Crassostrea gigas* contained up to 6480 mg/kg (Boyden and Romeril, 1974). On the other hand, crustaceans and molluscs from many other parts of Europe and North America bear level of  $\leq 60$  mg/kg.

Maximum residues are generally found in internal organs. Ireland and Wootan (1977) reported levels of 554 and 61 mg/kg in the digestive gland gonad and body of the marine gastropod *Thais lapillus* collected from the coasts of Wales while residues in the viscera of shrimp and squid from the Gulf of Mexico were 2-7 times greater than those of muscles (Horowitz and Presley, 1977). Some species, including gastropods *Helix aspersa* and *Littorina littorea* show relatively even distribution of Cu throughout their tissue (Coughtrey and Martin, 1976, Ireland and Wootan, 1977).

Rate of sorption by planktonic invertebrates generally depends on the copper concentration in water. In addition, uptake by benthic species is directly related to levels in sediments. Depending on species, low temperatures may reduce the rate of sorption. Similarly, uptake varies with salinity and the presence of other metals in solution.



## 2.2 TOXICITY OF COPPER

### 2.2.1 Fish

Copper is usually more toxic to fresh water fish than any other metal except Hg (Fig. 2.1) (Moore and Ramamoorthy, 1984).  $LC_{50}$ 's range from 0.017 to 1.0 mg/L under most conditions. However, unusually high water hardness may increase the 96h  $LC_{50}$  to 3.0 mg/L. Copper is much less toxic to marine fish due to the high complexing capacity of salt water. Approximately 30% mortality occurred in mammichog following exposure at 8.0 mg/L  $Cu\ L^{-1}$  for 96 h (Eisler and Gardner, 1973).

Acute toxicity to fresh water depends largely on hardness (Figure 2.1). Ionic copper ( $Cu^{2+}$ ) and ionized hydroxide ( $CuOH^+$ ,  $Cu_2OH_2^{2+}$ ) are not toxic, with a combined 96h  $LC_{50}$  of 0.0009-0.23 mg/L. At low hardness (12 mg/L) the incipient lethal concentration (ILC) of dissolved copper to rainbow trout was not affected by a change in alkalinity of 10-50 mg/L (Miller and Mackay, 1980). However, the same change in alkalinity in hardwater (98 mg/L) resulted in a 1.8-fold increase in the ILC.

Toxicity of combination of  $Cu^{2+}/CuOH^+/Cu_2^{2+}$  and  $H^+$  were antagonistic to rainbow trout at  $pH < 5.4$  whereas at  $pH > 5.4$  there was synergistic between copper toxicity and pH (Miller and Mackay, 1980). Synergistic effects have also been noted for combination of Cu/Cd/Zn, Cu/Zn, Cu/Zn/Ni, Cu/Zn/phenol and Cu/chloroamines. Antagonist effects occur following complexation with organic material, sewage and  $CaCO_3$ .

Exposure to chronic/sublethal levels (0.02-0.2 mg/L) of copper reduces survival growth and the rate of reproduction in a variety of species. In soft water, fecundity and egg survival may be inhibited at concentration as low as 0.004 mg/L. The hematocrit for a range of species of increases, with copper levels in the environment oxygen consumption, blood pH and the energy expenditure may also increase whereas feeding (Waiwood and Beamish, 1978, Lett et al, 1974). Sub-lethal exposures also result in behavior changes, such as decreased concealment and ability to orient.

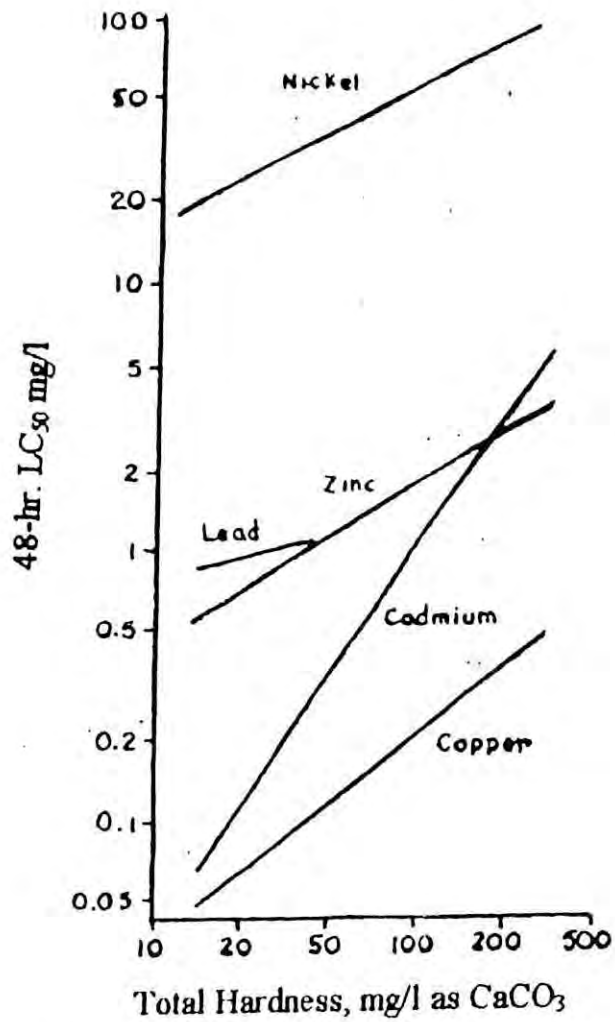


Fig. 2.1 : Correlation between total hardness of water and the 48h LC<sub>50</sub> for rainbow trout of nickel, zinc, cadmium, and copper. (From Brown, 1968)

Copper ions precipitate in gill secretions, causing death by asphyxiation (Tsai, 1979). There is also an impairment of haemopoietic tissue in gill filaments which results in reduction of oxidative activity. Necrotic kidney cells, fatty degeneration of the liver and brain hemorrhage have been reported for acutely exposed fish.

### **2.2.2 Aquatic Plants**

Copper is highly toxic to most aquatic plants. Inhibition of growth generally occurs at  $\leq 0.1$  mg/L, regardless of test conditions and species. Other effects, such as reduced carbon and silicic acid uptake, occur at copper concentration of 0.003-0.03 mg/L. Hg is the only metal which is consistently more toxic to aquatic plants than copper.

Sub-lethal effects of Cu intoxication include initial loss of potassium due to increased permeability of the cell. There may also be inhibition of oxygen evolution and assimilation of carbon and decrease in the rate of photosynthesis. Cell volume, particulate carbon and nitrogen levels and silicic acid uptake may be reduced at concentration below 0.05 mg/L.

Presence of complexing substances in water greatly reduces toxicity. Such agents generally originates from decaying matter. Many algal species can adopt to high copper levels in waters. Tolerant accumulate high levels (600 mg/kg dry-wt) of copper while still growing and dividing (Stokes, 1975), thereby increasing the amount of copper in the food chain in polluted waters.

### **2.2.3 Invertebrates**

Copper is highly toxic to most fresh water and marine invertebrates.  $LC_{50}$ 's are generally less than 0.5 mg/L through they may range from 0.006  $\geq$  225.0 mg/L under certain conditions. Toxicity is greater in fresh water than in marine waters, reflecting the relative proportion of the toxic free copper ions in solution.

Water hardness plays a role in determining toxicity. The  $LC_{50}$  for the oligochaete *Tubifex tubifex* increased by a factor of 150 when water hardness increased from 0.1 to 0.261 mg  $CaCO_3$  /L ( Brkovic-Popovic and Popovic, 1977). Similarly, toxicity of *Daphnia Magna* was directly related to copper, dissolved copper and inorganic chelator concentration (Andrew et. al., 1977).

The presence of organic chelators in solution significantly increased survival. Following exposure to 0.02 mg Cu/L, mortality in embryos of the pacific oyster *Crassostrea gigas* exceeded 97% (Knezovich et. al, 1981). However, the addition of humic matter and EDTA reduced mortality to 10.8 and 14.8% respectively. Furthermore, sand sorbs copper from solution, thereby decreasing availability of copper to the test organisms.

Treatment of polychaete *Eudistylia vancouveri* with 0.01 mg Cu/L caused a shortening and clubbing of the pinnules on the grill (Young et. al., 1981). There was a less cellular adhesion in the grills and structure derangement that lead to cell necrosis and death.

### 2.3 CHEMISTRY OF COPPER

Copper, one of the most mobile metals in environment is toxic to human at high level of concentration. It has two oxic states; i) Cuprous copper and ii) Cupric copper. Usually, cuprous copper is unsuitable in aerated water over the general pH range (pH 6-8) of natural water and is readily oxidized to cupric state. In natural aquatic system copper exist in three physical states:

Particulate state: Particulate matters include oxide, sulfide, and malachite ( $Cu_2(OH)_2CO_3$ ) precipitates, as well as insoluble inorganic and organic complexes and copper adsorbed on clay or other mineral solids .

Dissolved state: Dissolved state includes free cupric ion and soluble complexes. Bivalent copper chloride, nitrate, sulfates are highly soluble in water.

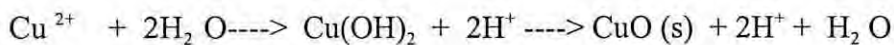


Colloidal state: Colloidal states of copper are polypeptide materials, fine clay and metallic hydroxides precipitates. Copper carbonate, cupric hydroxide, oxide, and sulfide precipitate out or form colloidal suspension in presence of excess cupric ions.

Copper forms complexes with hard bases like carbonate, nitrate, sulfate, chloride, ammonia and hydroxide. Neutral ligands such as ethylenediamine, ammonia and pyridine form strong complexes with copper. Copper interacts strongly with sulfur, forming relatively stable insoluble sulfides. Being an intermediate acceptor between hard and soft acids, copper complexes with nitrogen and sulfur containing legands. Humic materials in freashwaters bind more than 90% of total- Cu whereas those in seawater bind only 10%. In the latter case calcium and magnesium, because of their large concentrations, displace copper from humic materials.

Fate of copper in the aquatic and marine environment is governed by the process of complex formation with inorganic and organic legands. Organic acids also cause mobilization of copper from sediment into the overlying water (USEPA,1984). As copper has high affinity to hydrous ion, manganese oxide, clay carbonate minerals and organic matter; sorption of these materials in water or in sediment increases the solid phase concentration and reduces the dissolved phase concentration in the system. Other factors governing the speciation and precipitation of copper in an aquatic system are pH, alkalinity, temperature and concentration of other chemical components. Two precipitation reactions of copper under thermodynamic equilibrium are;

- a. Precipitation of cupric hydroxide followed by conversion of hydroxide to oxide



- b. Precipitation of malachite



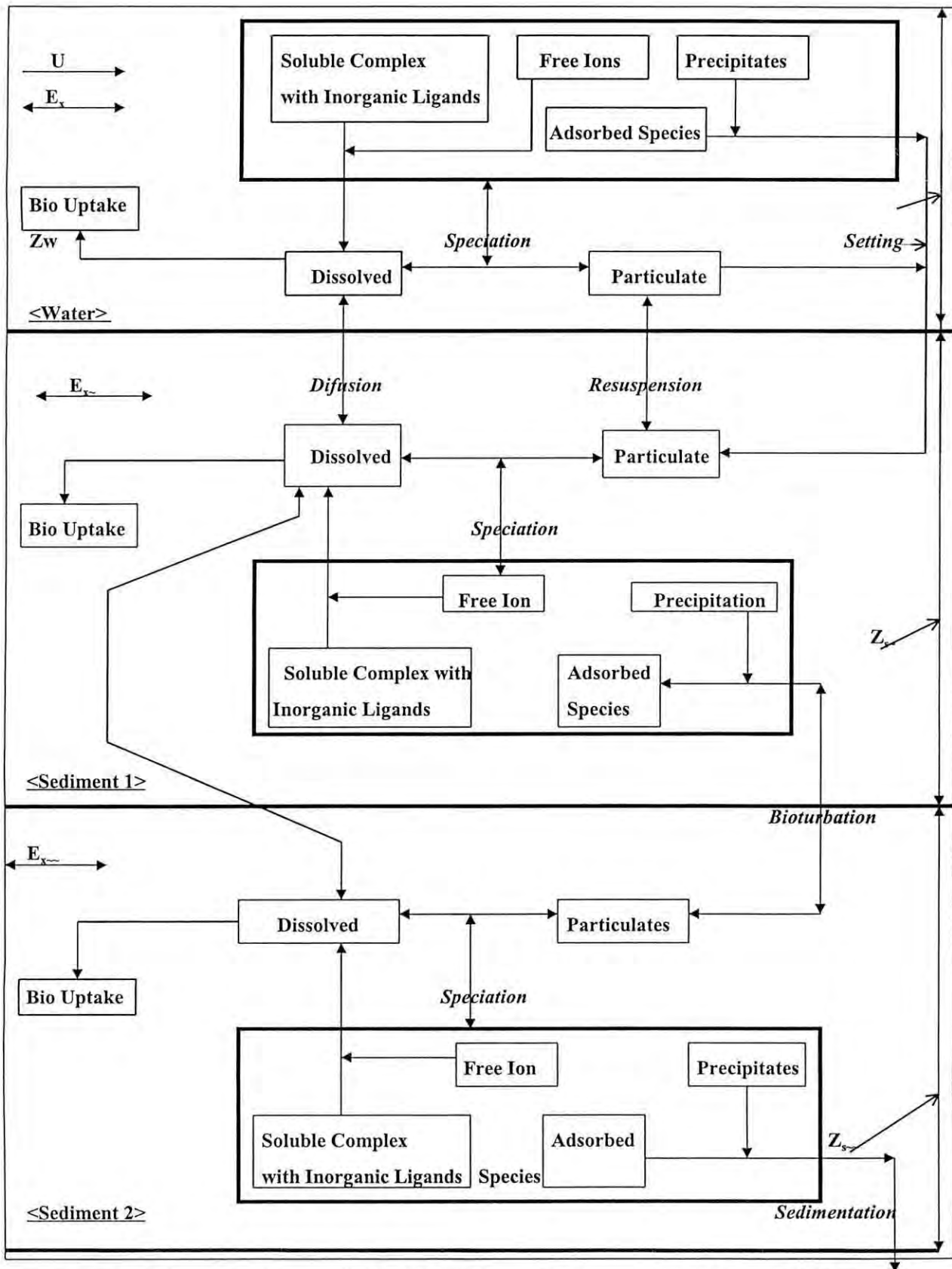


Fig. 2.2 : Schematic diagram for Cu(II) pathways (Badruzzaman and Lung,1992)

Both reactions are dependent on pH values and on the bicarbonate (alkalinity) concentration of the solution. Based on equilibrium calculations, malachite is usually the only precipitated specie in the pH range of most fresh waters. In the presence of copper precipitates, the free cupric ion can further complex with bicarbonate ions to form soluble  $\text{CuCO}_3$  species. This explains why the concentration of free cupric ion only represents a small fraction of the total soluble copper. Table 2.1 represents a few of the reactions of Cu(II) with ligands and the corresponding equilibrium constants pertinent to formation (USEPA, 1987).

Toxicity of copper: In natural waters metal like copper readily form stable hydroxyl or carbonate complexes or both - and only a fraction of total concentration exists as cationic or aquo form. The most important species of copper causing toxicity are  $\text{Cu}^{2+}$ ,  $\text{Cu(OH)}^+$  and  $\text{Cu(OH)}_2$  aq. (Chakoumakos et al, 1979). Mortality rates and reciprocal survival times of aquatic lives were directly related with cupric ( $\text{Cu}^{+2}$ ) and copper hydroxyl ( $\text{Cu(OH)}_2$ ) ion activities as determined by equilibrium calculations. The concentration of these species varies with pH and alkalinity. At lower alkalinity the main species formed are  $\text{CuHCO}_3^+$ ,  $\text{CuCO}_3^0$  and  $\text{Cu(CO}_3)_2^{2-}$  which show no visible toxicity. Small changes in DO,  $\text{CO}_2$  content, pH, alkalinity, hardness of water alter both the aqueous chemistry of the toxicant and the animals physiological response to that toxicant. The toxicity of copper to rainbow trout was found to be related to the total concentration of Cu and  $\text{CuCO}_3$  (in the absence of organic complexes) rather than to the concentration of either of these forms alone. Addition of orthophosphate resulted in decreased solubility of copper and a corresponding decrease in toxicity. Pyrophosphate, however, increased copper solubility but resulted in a nearly complete removal of toxicity (Andrew, Biesinger and Glass, 1976).

Toxicity increases with increasing pH (Mount (1966), Steeman (1969), Mancy and Allen, 1976). Formation of either inorganic or organic complexes greatly reduces metal toxicity. Reduction in toxicity is related to the stability constant of the metal complexes formed (Nishikawa and Tabana, 1969). Zinc and copper solutions with an excess of strong chelating agents EDTA is much less toxic to fish and aquatic invertebrates. Similarly, thiosulfate, citrate, glycerin and humic acids reduce toxicity in proportion to

Table 2.1 : Equilibrium Constant for copper (USEPA, 1987)

| Ligand                        | Log K  | Equation and Comments  |
|-------------------------------|--|--|
| OH <sup>-</sup>               | 6.37   | $\text{Cu}^{2+} + \text{OH}^- = \text{CuOH}^+$                       |
|                               | 6.21   | $\text{Cu}^{2+} + \text{OH}^- = \text{CuOH}^+$ (pH=3.4)              |
|                               | 11.70  | $\text{Cu}^{2+} + 2\text{OH}^- = \text{Cu}(\text{OH})_2$ (pH=8.4)    |
|                               | 14.30  | $\text{Cu}^{2+} + 2\text{OH}^- = \text{Cu}(\text{OH})_2$             |
|                               | 15.00  | $\text{Cu}^{2+} + 2\text{O}^- = \text{Cu}(\text{OH})_3$              |
|                               | 16.00  | $\text{Cu}^{2+} + 4\text{OH}^- = \text{Cu}(\text{OH})_4^{2-}$        |
|                               | 17.70  | $2\text{Cu}^{2+} + 2\text{OH}^- = \text{Cu}(\text{OH})_2^{2+}$       |
| Cl <sup>-</sup>               | 0.02   | $\text{Cu}^{2+} + \text{Cl}^- = \text{CuCl}^+$                       |
|                               | 2.05   | $\text{Cu}^{2+} + \text{Cl}^- = \text{CuCl}^+$                       |
|                               | -0.71  | $\text{Cu}^{2+} + 2\text{Cl}^- = \text{CuCl}_2$                      |
|                               | -2.30  | $\text{Cu}^{2+} + 3\text{Cl}^- = \text{CuCl}_3$                      |
|                               | -4.60  | $\text{Cu}^{2+} + 4\text{Cl}^- = \text{CuCl}_4$                      |
| F <sup>-</sup>                | 1.26   | $\text{Cu}^{2+} + \text{F}^- = \text{CuF}^+$                         |
| CO <sub>3</sub> <sup>2-</sup> | 5.97   | $\text{Cu}^{2+} + \text{CO}_3^{2-} = \text{CuCO}_3$ (aq)             |
|                               | 6.00   | $\text{Cu}^{2+} + \text{CO}_3^{2-} = \text{CuCO}_3$ (aq)             |
|                               | 6.34   | $\text{Cu}^{2+} + \text{CO}_3^{2-} = \text{CuCO}_3$ (aq)             |
|                               | 6.30   | $\text{Cu}^{2+} + \text{CO}_3^{2-} = \text{CuCO}_3$ (aq)             |
|                               | 6.80   | $\text{Cu}^{2+} + \text{CO}_3^{2-} = \text{CuCO}_3$ (aq)             |
|                               | 6.20   | $\text{Cu}^{2+} + \text{CO}_3^{2-} = \text{CuCO}_3$ (aq)             |
|                               | 10.30  | $\text{Cu}^{2+} + 2\text{CO}_3^{2-} = \text{Cu}(\text{CO}_3)_2^{2-}$ |
| 9.83                          | $\text{Cu}^{2+} + 2\text{CO}_3^{2-} = \text{Cu}(\text{CO}_3)_2^{2-}$ |  |
| S <sup>2+</sup>               | 40.00  | $\text{Cu}^{2+} + \text{S}^{2-} = \text{CuS}$                        |
| SO <sub>4</sub> <sup>2-</sup> | 2.25   | $\text{Cu}^{2+} + \text{SO}_4^{2-} = \text{CuSO}_4$ (aq)             |
| HS <sup>-</sup>               | 26.00  | $\text{Cu}^{2+} + 3\text{HS}^- = \text{Cu}(\text{HS})_3^-$           |
| CN <sup>-</sup>               | 25.00  | $\text{Cu}^{2+} + 4\text{CN}^- = \text{Cu}(\text{CN})_4^{2-}$        |



the concentration the added chelant (Grande (1966), Sprague (1968), Tabata and Nishikawa (1969) and Biesinger et. al. (1973).

## 2.4 METAL SPECIATION

### 2.4.1 Speciation of Metals in Aquatic Environment

The first step to determine the chemical equilibrium composition in an aquatic environment is to ascertain the approach in solving the equilibrium problem. Generally two different approaches are being used :

1. Minimization of the system free energy under mass balance constraint.
2. Simultaneous solution of the nonlinear mass action expressions and linear mass balance relationship.

According to Van Zeggren and Storey (1970) these two methods are to be mathematically equivalent. The second approach is more frequently used and is referred to as the “equilibrium constant method”. In this method, the chemical equilibrium problem is described as a set of mass balance equations, one for each component, and a set of mass action equations, one for each specie. Then these non-linear mass action equations are solved using the mass balance equations. The equilibrium composition of the aquatic environment is determined by the minimization of the Gibbs free energy of the system within the mass balance constrains. The chemical equilibrium determines the aqueous metal speciation in addition to the effects of precipitation/dissolution and sorption. A system containing  $j$  components can be represented by a set of  $j$  mass action expressions as follows :

$$Y_i C_i = K_i \prod_{j=1}^{j=n} X_j^{a_{ij}}$$

where,

$Y_i$  = activity coefficient of specie i

$C_i$  = concentration of specie i

$K_i$  = formation constant for specie i

$X_j$  = activity of component j

$a_{ij}$  = stoichiometric coefficient of component in specie i

$n$  = number of components .

In logarithmic form the equation becomes;

$$\log C_i + \log Y_i = \log K_i + \sum_{j=1}^{j=n} a_{ij} \log X_j$$

In addition to the mass action expression, the system of j components is governed by total number of j mass balance equations of the form ;

$$T_j = \sum_{i=1}^{j=s} a_{ij} C_i$$

Where

$T_j$  = total analytical concentration of component j

$s$  = number of aqueous species

An iterative numerical technique is usually used to solve these equations. Most commonly used iterative technique for this purpose is the Newton Raphson method. To arrive a solution, an error term ( $y_i$ ) is defined such that,

$$y_i = \sum_i a_{ij} C_i - T_j$$

Where ,

$y_i$  = the error or remainder in the mass balance equation for each component j

The final solution is reached when the following criteria is met ;

$$|y_i| \leq \text{convergence criteria (e.g. ; .001)}$$

These mass action and mass balance equations are for a system with no solid phases. Solid phases such as precipitates, are handled by “transformation of basis” method, which reduces the degree of freedom by the number of solids while solving the simultaneous equations. However, using these chemical equilibrium concept requires enormous amount of thermodynamic and component data of the metals and species and the species under consideration. Most of the computer programs available for the computation of chemical equilibrium composition have extensive collection of these data.

#### 2.4.2 Approaches for Metal Speciation Analysis

Chemical equilibrium problems involving only a few species which can be solved manually by using mass law and mole balance equations and charge balance equations. This is often done by making simplifying assumption and using log concentration diagrams. However, for more complex problems, as for example, where many species are involved (say more than 15 to 20), where several solids are present, and where equilibrium between the atmosphere and water must be considered (open system), computer solutions are required. Most of the computer programs available basically solve the mass balance and mole balance equations simultaneously by using various convenient systems. In general there are two basic approaches as mentioned earlier are

- 1) Direct minimization of Gibbs free energy, and
- 2) Equilibrium constant approach.

Equilibrium constant approach is more widely used for solving chemical equilibrium problems. Basic solution scheme for equilibrium constant approach is as follows.

- Choose a set of components: components are a set of chemical entities that can be used to provide a complete and unique stoichiometric formula for each chemical species in the system.
- Specify total concentration for components.
- Guess final concentration of components.
- Calculate Gibbs free energy composite of system from the equilibrium constant.
- Solve mass-balance equation by iteration.

According to this approach, a set of components is first defined in such a way that every species of the system can be written as the product of a reaction involving only the components. So components can be written as the product of a reaction involving the other components. Chemical equilibrium problem involving components,  $M^{2+}$ , HL and  $H^+$  (here,  $M^{2+}$  represents any metal ion,  $H^+$  hydrogen ion and L any anionic ligand), can be taken as an example. Possible species that can be formed by above components are  $M^{2+}$ ,  $MOH^+$ , HL,  $ML^+$  and  $OH^-$ . The mass action equations for these species are:

$$[M^{2+}][H^+]^{-1} K_1 = [MOH^+]$$

$$[HL][H^+]^{-1} K_2 = [L^-]$$

$$[M^{2+}][HL][H^+] K_3 = [ML^+]$$

$$[H^+]^{-1} K_4 = [OH^-]$$

where,  $K_1$ ,  $K_2$ ,  $K_3$ ,  $K_4$  are equilibrium constants of the above equations. Algebraic description of the above equilibrium problem can be given as follows:

$$T = [T_M \ T_{HL} \ T_H]$$

$$X = [[M^{2+}] \ [HL] \ [H^+]]$$



$$A = \begin{bmatrix} 1 & 0 & 0 \\ 1 & 0 & -1 \\ 0 & 1 & 0 \\ 0 & 1 & -1 \\ 1 & 1 & -1 \\ 0 & 0 & 1 \\ 0 & 0 & -1 \end{bmatrix} \quad C = \begin{bmatrix} [M^{2+}] \\ [MOH^+] \\ [HL] \\ [L^-] \\ [ML^+] \\ [H^+] \\ [OH^-] \end{bmatrix} \quad \text{and} \quad K = \begin{bmatrix} 1.0 \\ K_1 \\ 1.0 \\ K_2 \\ K_3 \\ 1.0 \\ K_4 \end{bmatrix}$$

Where, T = Total concentrations of components  
X = Free concentrations of components  
A = Stoichiometry matrix  
C = Concentrations of species  
K = Stability constants of species

The next step for solving chemical equilibrium problem is to specify the total concentrations of each component (T). Initial guess for X is then made. Concentrations of species (C) are then computed using mass law equation :

$$\log C_i = \log K_i + \sum_j a_{ij} \log X_j + a_{H_2CO_3}$$

where, i = 1 to M and M = Number of linear independent constrains (representing conservation of mass and charge balance equation), and j = Number of species.

From species concentration (C<sub>i</sub>) error in material balance equation for each component is then computed using following equation:

$$Y_i = \sum_j a_{ij} C_i - T_j$$

Then an improved guess for X is obtained by using the multi-dimensional Newton-Raphson iteration technique. Iteration procedure is carried out until error in material balance equations (Y) is small.

Various computer programs (e.g., MINTEQA, MINEQL +, MICROCOL) are available for chemical equilibrium analysis of complex systems. MINEQL+ uses an approach similar to that described above. The solution procedure of an equilibrium problem using MINEQL+ can best be described by the following flow chart :

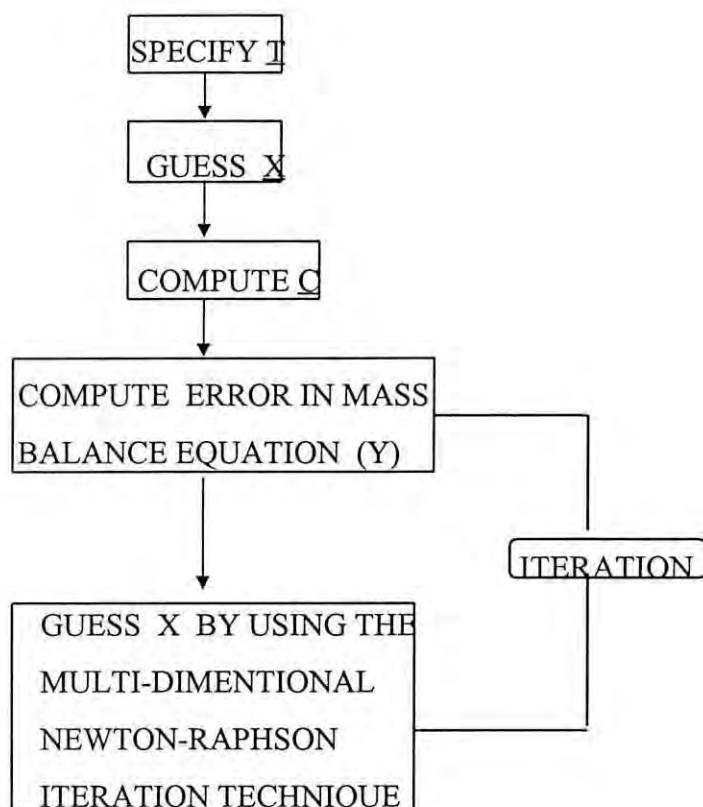


Fig. 2.3 : Flow chart for solving equilibrium problem using MINEQL<sup>+</sup>

## 2.5 COPPER PATHWAYS IN WATER AND AQUATIC SEDIMENT

The distinguishing property of many toxic substances is their affinity to surfaces, which is provided by the solids in suspension and in the bed. The sorptive interaction between the dissolved and particulate components tends to a state of equilibrium. The time required to achieve this condition may vary markedly depending on the characteristics of

the chemical and sorbent. If the rate at which equilibrium is achieved is much faster rapid than the other kinetic routes indicated, i.e. decay, volatilization, settling and exchange with the bed, a state of instantaneous equilibrium may be assumed. The settling and exchange factors lead to an expression that relates the concentration of the chemical in the water and the bed. The principal physical and chemical phenomena are

1. Sorption and desorption between dissolved and particulate forms in the water column and sediment .
2. Settling and resuspension mechanisms of particulates between the sediment and the water column .
3. Diffusive exchange between the sediment and the water column .
4. Loss of chemical due to biodegradation, volatilization, photosynthesis and other chemical and biochemical reactions .
5. Gain of the chemical due to chemical and biochemical reactions .
6. Transport of the toxicant due to advective flow transport and dispersive mixing .
7. Net deposition and loss of chemical to deep sediment .

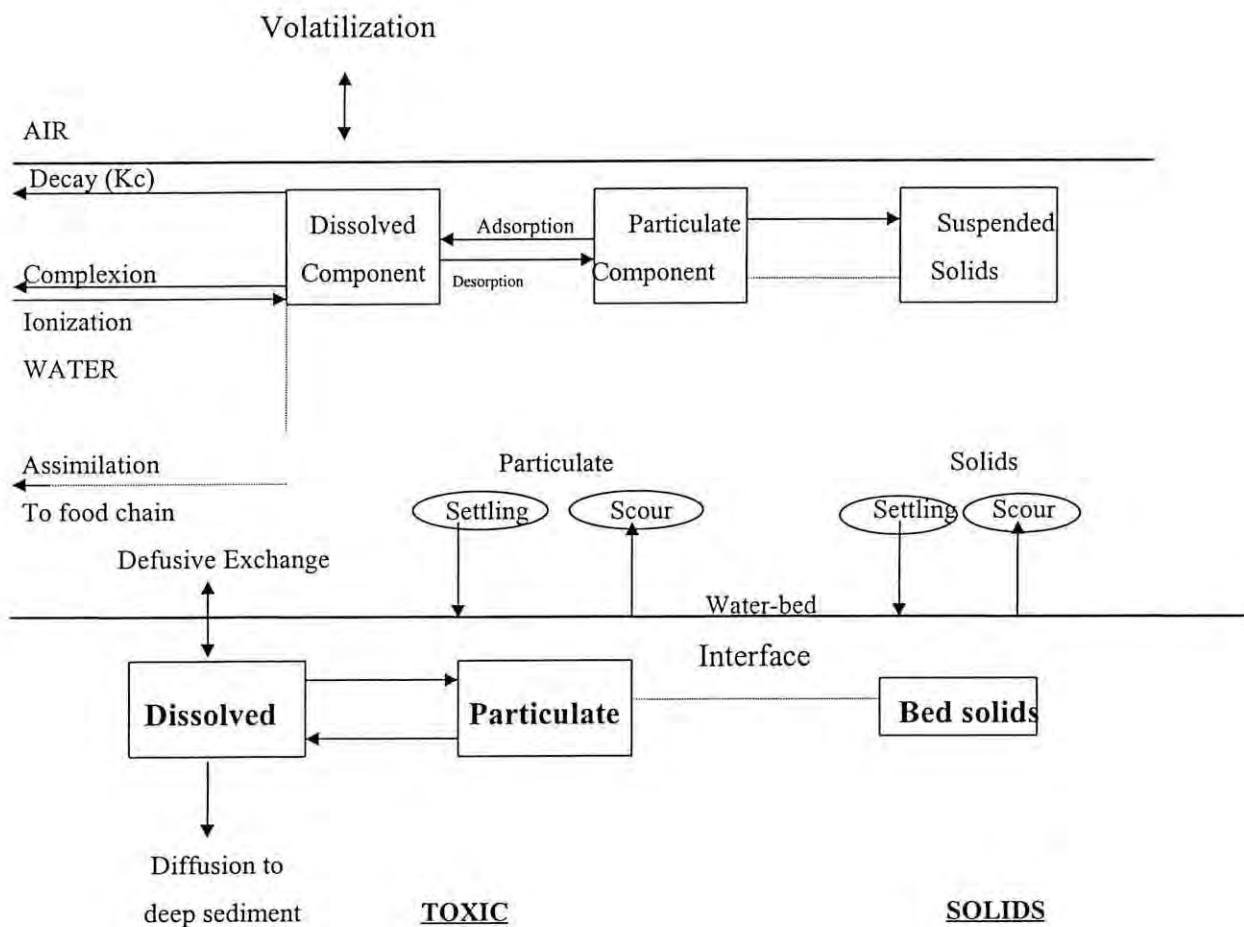


Fig.2.4 : Schematic diagram for Cu(II) pathways.

## 2.6 LITERATURE REVIEW

### 2.6.1 Case Study

#### *Sedimentary Evidence for Decreased Heavy-Metal inputs to the Chesapeake Bay*

The study was performed by Owens and Cornwel (1995) to determine whether two decades of environmental regulations have made a difference in deposition of the amount of trace metal in Chesapeake bay.

In this study two assumptions were adopted to assess the accumulation of heavy metal in the system, those are :



1. Age of the sediment is known
2. Concentration of heavy metal reflect the temporal input function .

Two sampling sites were chosen in Chesapeake bay. Undisturbed box cores of 50 cm were taken with 15 cm diameter acrylic tubes. The cores taken from two sampling sites consisting of soft fluid sediments and were dried at a temperature of 65<sup>o</sup> C for 4 days. Then the sediment samples were grounded. All trace metal samples were digested in aqua regia. Trace metal analysis were carried out via flame Atomic Adsorption Spectrophotometer, with deuterium background correction.

Sedimentation rates were calculated using both Constant Initial Contraction model (CIC) and Constant Rate of Supply model (CRS). The CIC model assumes that sedimentation rate and flux of <sup>210</sup>Pb to the sediment are both constant while CRS model requires constant <sup>210</sup>Pb fluxes, but accommodates variable sedimentation. Cumulative mass ( gm cm<sup>2</sup> ) was used as the depth scale for estimating the mass sedimentation rate (gm m<sup>2</sup> yr<sup>-1</sup> ).

In this study, it was found that mid bay channel sediments experience seasonal anoxia which minimizes activity of bioturbating organism. In modern sediment, there is absence of biological structures. Sediment resuspension is moderate in mid bay channel sites. Pore water analysis show high concentration of hydrogen sulfide, several cm into the sediment. On the basis of solubility products of metal sulfides, the metal should be immobile after being buried below the top few cm of sediment, solution complexes with sulfur and organic matter may enhance metal solubility.

Sediment copper, zinc and lead profiles from both cores followed same pattern beginning with a steady increase from the early 1900s to late 1970s. Lead concentration in both cores peak in the mid 1970s and then drop off sharply to the present. In case of copper and zinc, concentration maximum occurs several years earlier than that of lead. Core of both stations have “ Pb profile ” that are generally exponential. Evidence that the subsurface Pb peak is not a diagenetic feature is found by comparing these data with

those collected with the previous study 16 years earlier. Other studies from the 1970s show similar profiles. The 1975 data show a near surface peak in Pb concentration, consistent with 1991 cores which show a subsurface peak corresponding to the mid 1970s. As with Pb peak concentrations are found in the 1960s-1970s time frame, with the lower part of our profiles consistent with those collected in 1975.

Profiles for copper, lead, zinc showed an increase in metal concentrations from the beginning of the century to the early 1970s, and a decrease in more recent years. So it shows that significant progress has been made in decreasing trace metal contamination in the mainstem Chesapeake Bay.

#### *Trace metal speciation in the Yamaska and St. Francois rivers (Quebec)*

This study was done by Tessier, Campbell and Bisson in 1979. Water and suspended sediment samples were collected at 12 stations on Yamaska and St. Francois rivers. In this study metal concentrations in filtered water samples were determined by atomic adsorption spectrophotometry and quantitation was achieved by a standard addition technique. Suspended sediment samples were subjected to sequential extraction procedure designed to partition the particulate trace metals into five fractions :

1. Exchangeable metals (fraction 1): sediment sample was extracted for 10 minutes with 1M MgCl<sub>2</sub> at pH 7 .
2. Metals bound to carbonates (fraction 2): is the residue from fraction 1 leached for 5h with 1M NaOAc adjusted to pH 5.0 with acetic acid .They may be associated with sedimentary carbonates, either as separate phases or in structural positions within calcium or magnesium carbonates.
3. Metal bound to Fe-Mn oxides ( fraction 3 ) : is the residue from fraction 2 was extracted for 6h at 96 °C with 0.04 M NH<sub>2</sub>OH.HCl in 25% V/V HOAc and are associated with Fe and Mn oxides.

4. Metal bound to organic matter ( fraction 4 ) : is the residue from fraction 3 was extracted at 85 °C for 5h with 30% H<sub>2</sub>O<sub>2</sub> adjusted to pH 2 with HNO<sub>3</sub> and then at room temperature with 3.2 M NH<sub>4</sub>OAC in 20% (V/V) HNO<sub>3</sub>

5. Residual Metals ( fraction 5 ) : The residue from fraction 4 is dried and fused with lithium metaborate ; the fused material was dissolved in a minimum amount of 12N HCL and then diluted to a final acid concentration of 1.2 N and are associated with detrital silicate minerals, resistant sulfides, and refractory organic materials.

Analysis of the results obtained in this study indicate that total soluble and particulate trace metal concentrations present great spatial and temporal variations as do levels of suspended solids. Distribution of a given metal among the various fraction of the particulate matter is relatively constant.

Copper was found predominantly in soluble forms. Mean concentration of dissolved copper in the Yamaska and St. Francois river basins were 1.2 and 8.6 ug/l respectively. Total particulate copper are found in the residual (41 & 22%), Fe-Mn oxides (20 and 12%) and carbonate (8 and 14%) fractions whereas much lower percentages are found in the exchangeable fraction (1 and 1.2%). Particulate copper distribution is the percentage of the total metal bound to organic matter (31 and 52%) because - for most legands copper exhibits the highest stability constants of all the metal considered.

Sequential extraction process of the present study highlights areas where anomalously high concentrations of particulate trace metals may adversely affect water quality and biota . Application of the procedure to suspended sediment samples yielded reasonably constant trace metal speciation patterns for each metal.

#### ***Water Quality Modeling (Speciation Modeling of Copper) in South San Francisco Bay***

The study in South Sanfrancisco Bay, California was conducted by Kevin J. Novo Gradac and P.F. Wang in 1984 because of increased concentration of metal and, thus an increased bio-availbility to Bay organisms. A scheme for estimating the distribution of copper

among dissolved and adsorbed phases as well as the process controlling the partitioning of copper using geochemical speciation model MINTQA2 was used.

The diffuse-layer methodology and constants from Dzombak (1986) had shown to yield excellent results when modeling copper sorption to an amorphous iron oxyhydroxide phase. In the present study it was assumed that amorphous iron oxyhydroxide phase would be able to sorb copper more strongly than would particulate organic matter.

A dataset having particulate organic matter (POC), dissolved organic matter (DOC), dissolved copper, suspended particulate matter, published by Kuwabara et. al. (1989) was used. The values were reported for a total of 20 different samples that varied spatially and temporally. The parameters from their dataset were used to calculate  $\text{mol}_{\text{Fe}1}$ ,  $\text{mol}_{\text{Fe}2}$  (site densities), DOC,  $\text{Cu}_{\text{total}}$  for three different  $f_{\text{Fe}}$  (weight fraction of Fe in the sediment) values that are employed in MINTEQA2 modeling. A number parameters were held constant including constant pH of 7.9 and the solution was assumed to be in equilibrium with carbon dioxide in the atmosphere.

The percentage of dissolved copper was predicted by MINTEQA2 for three scenarios of amorphous iron content ( 3.15, 4.15, 8.3 g Fe/kg ) in the suspended sediments are compared to measurements published by Kuwabara et al. (1983). The predicted values are within 1% of the actual values which indicate errors in predicted percentages of dissolved copper are small enough to adequately model the distribution of copper based on - DOC, suspended sediments,  $\text{Cu}_{\text{total}}$  and dominant sorbent for copper in the suspended sediments is an amorphous iron oxyhydroxide phase.

In case of speciation of copper the model predicts a number of dissolved copper species which are  $\text{Cu}^{+2}$  (2.3%),  $\text{Cu}(\text{OH})_2_{(\text{aq})}$ , (65.4%),  $\text{CuCO}_3_{(\text{aq})}$  (3.5%), Cu-sorbed (22.5%), Cu-DOC complex (4.5%). Since organic carbon copper complex is less than 5% of the total copper, it can be assumed that DOC is not very important toward modeling of copper distribution and an iron hydroxide phase controls the amount of dissolved copper levels.



### 2.6.2 Other Studies:

Sylva (1976) studied the copper speciation in aquatic systems by considering inorganic and organic complexation, adsorption and precipitation processes. The author investigated a given aquatic system with fairly known chemical composition and equilibria collected from literature. Analytically, the equilibrium condition was achieved by simultaneously solving the equilibrium mass balance equations using a modified version of computer program COMICS.

The major findings from Sylva's (1976) study are that in the absence of organic complexing agents, hydrolysis and precipitation are the reactions dominating the chemistry of copper in the pH range of the natural aquatic system. According to the author, the major process of removal in this case was precipitation of malachite which was affected by the pH of the system. The kinetics of this process was relatively slow. The author however inferred that the chemistry of a system changes to a greater extent depending on the presence of organic substances. Thus speciation of copper can be expected to vary from system to system and within one system over a period of time. According to Sylva (1976) adsorption processes biotic and abiotic, are expected to remove soluble copper from the aquatic system very rapidly. He concluded that in most aquatic systems the processes of adsorption and precipitation are capable of reducing free copper levels to very low concentration even if the initial concentration is very high.

Kuwabara et. al. (1989) studied the seasonal and spatial distribution of copper, zinc and cadmium for south San Francisco Bay. According to their study copper levels in water were related to the inherent dissolved organic carbon and is controlled by complexation. They also observed a reverse correlation between dissolved copper and salinity and concluded that the level of dissolved copper concentration is directly related to the sorption process.

Geesey et. al. (1984) studied the effect of river flow on distribution of copper species and other metals in Still Creek and the Fraser river in British Columbia. The author

concluded that an increased river flow rate would result a loss of soluble reactive copper from the sediment into the water column. A reversal of the situation will occur if the flow were reduced, as a result soluble reactive copper will increase in the sediment with the reduction of river flow.

A number of investigative research has been performed to assess the distribution of heavy metal in water and sediment. Bradford and Luoma (1980) studied the concentration of copper, zinc, amorphous iron, and organic carbon in oxidized surface sediments of the South Bay. According to their report, the southern most region of south bay was most heavily contaminated with copper and zinc. The area was identified to have the slowest circulation. It was found that the copper concentration is related to parameters such as percent of clay particles, amount of organic material and amorphous iron. The major portion of copper data obtained could be expressed with a regression equation as a function of particle size and amorphous iron.

Knowledge gathered from the literature review helped in the methodology of collection, preservation, and analysis of samples of water and sediment of this study.

## **CHAPTER- 3**

### **METHODOLOGY**

In this study, water and sediment samples were collected from different key locations of the Ramna and the Dhanmondi lakes. Some of the water quality parameters were tested in-situ and rest of the water quality parameters and the sediment quality were measured at the Environmental Engineering Laboratory of BUET. Locations of the two lakes can be found in the map of Dhaka city.

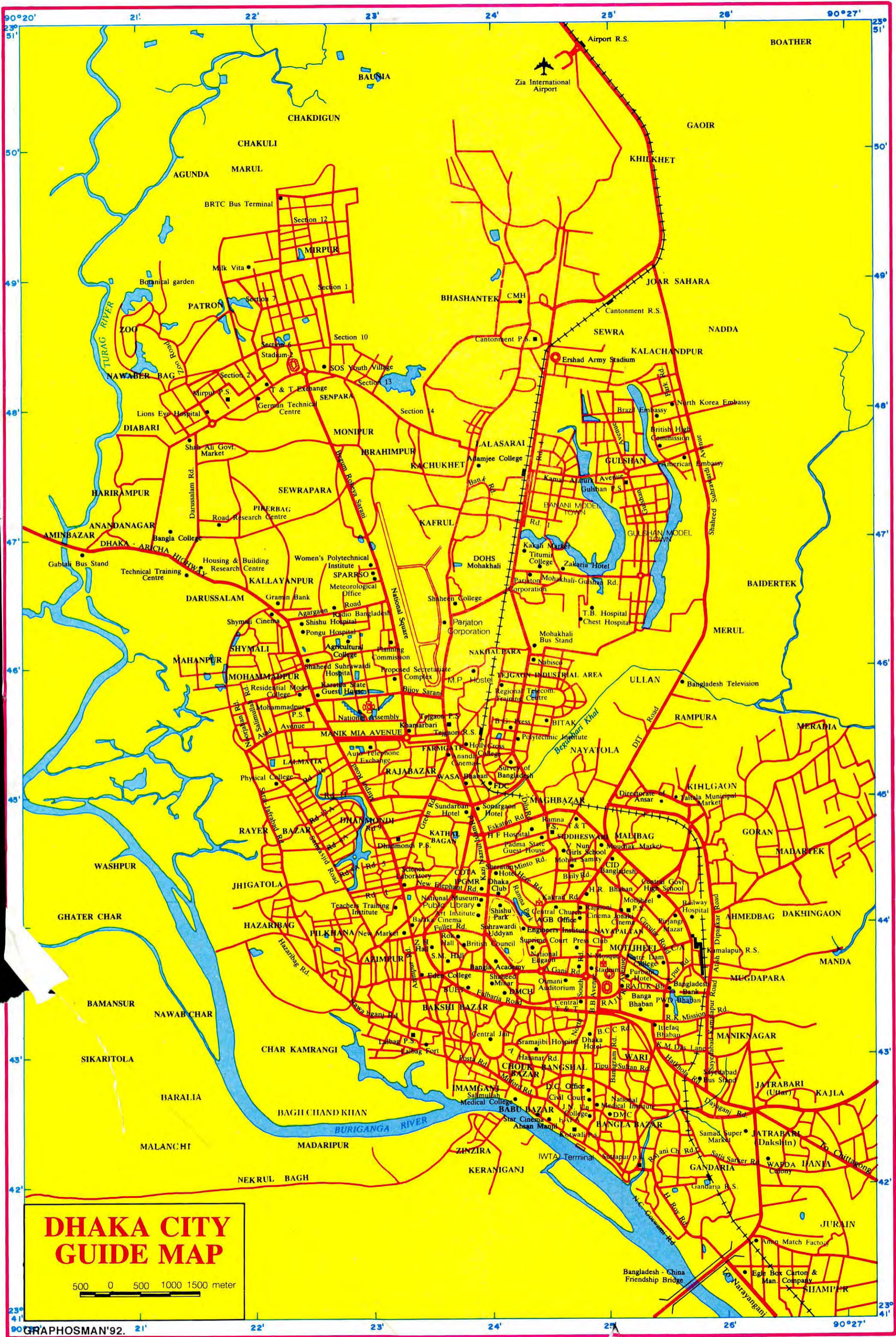
#### **3.1 SAMPLING LOCATIONS**

Selecting the number of sampling sites of the water body depends on number of factors such as frequency of sample collection, physical limitation of the laboratory, spatial variation of pollutant, number of sewage inlet into the lake. Selection of sampling location was based on the following criteria:

- i) Sampling locations should be chosen such that water samples are adequately representative of the system as a whole. In this respect, these zones or areas should be selected where it is expected that complete mixing of influent stream has occurred.
  
- ii) Sampling locations should be selected in such a way that they cover the entire lake in order to obtain a clear understanding of the spatial variation of water and sediment characteristics.
  
- iii) Samples should be collected from all locations that are in close proximity of the inlet points of the lakes

At the Ramna lake, water samples were collected from four preselected sites and in the Dhanmondi lake sample were collected from seven sites as shown in Fig. 3.1 and 3.2. Sediment samples were collected from key points (1 and 3) in Ramna lake and three points (2,3,7) in Dhanmondi lake.





# DHAKA CITY GUIDE MAP

500 0 500 1000 1500 meter



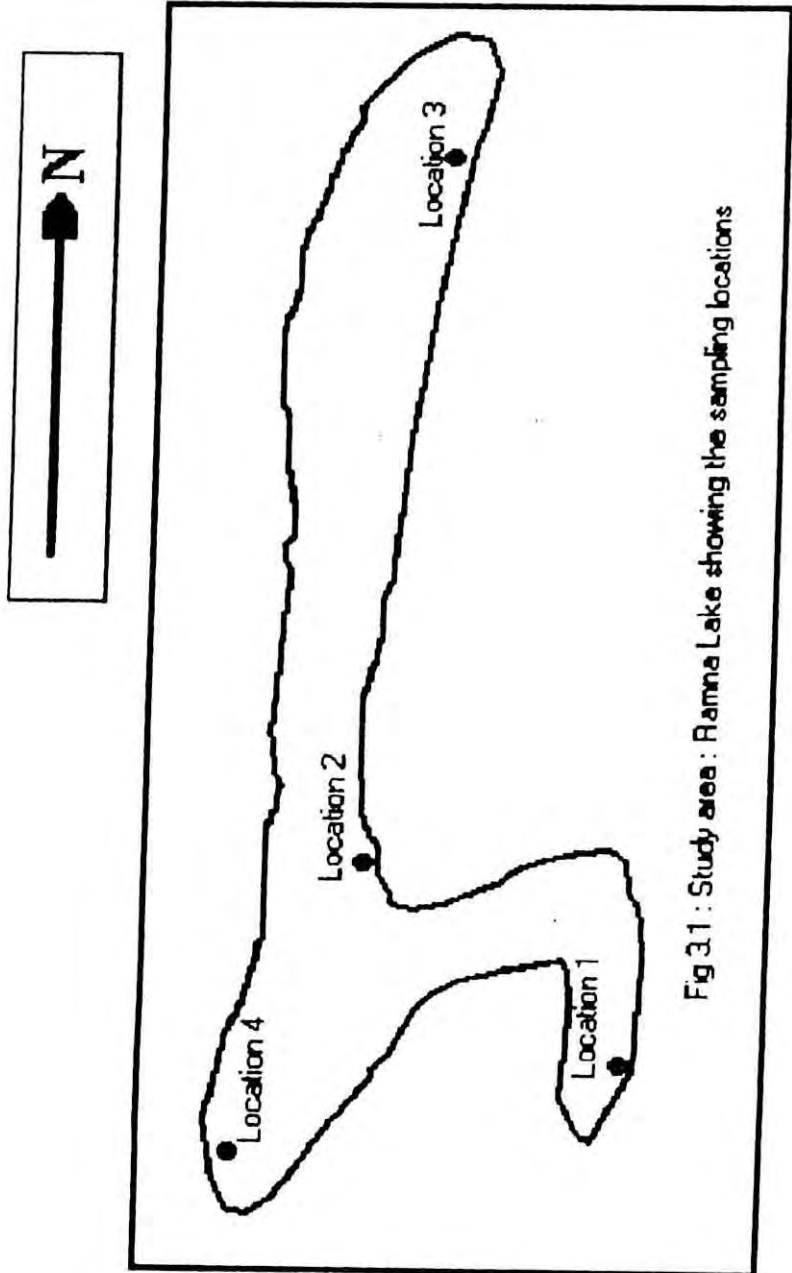


Fig 3.1 : Study area : Ramna Lake showing the sampling locations



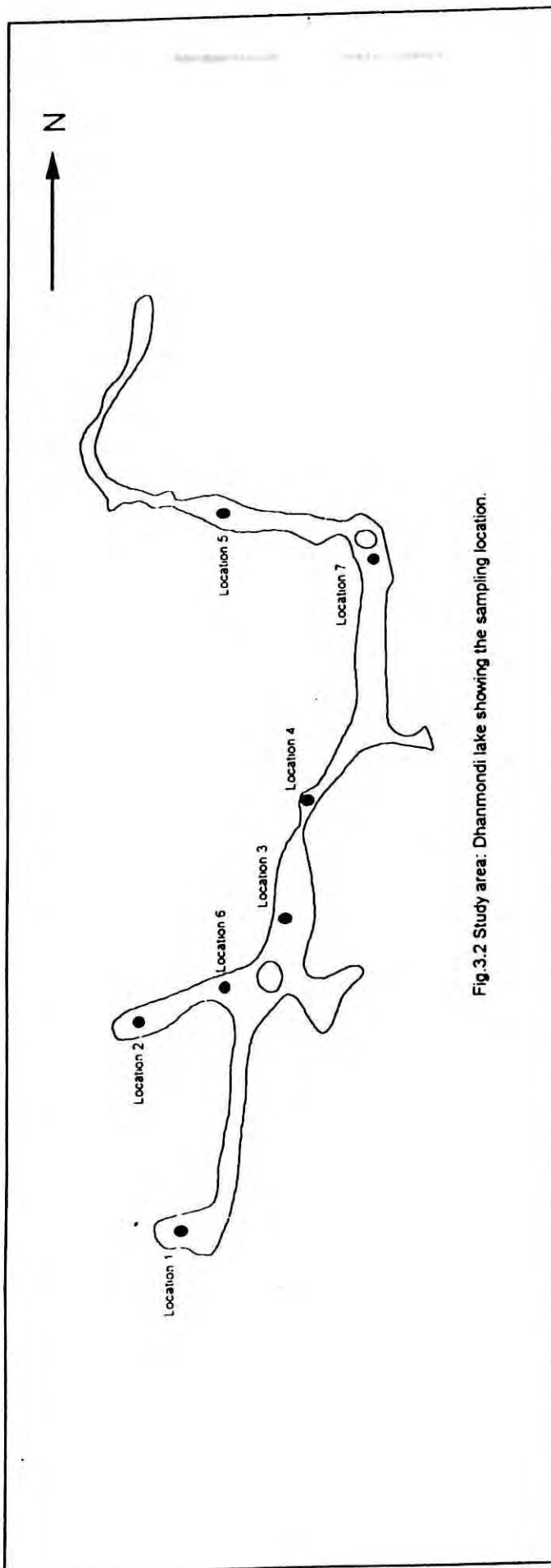


Fig.3.2 Study area: Dhanmondi lake showing the sampling location.

### **3.2 SAMPLING PROGRAM**

The composition of natural water of lakes and reservoir is always changing. Sometime the variation in composition is periodic (daily, seasonal, etc.). Seasonal variation in composition is mainly caused by rainfall, runoff, scorching sunshine, inflow from other sources (e.g. stream, industrial effluents, sewage, etc.). Daily variation in composition is due to biological process as needing the presence of sunlight. The water quality of lakes and reservoirs are greatly influenced by rainfall, runoff, and flow from tributaries. In the present study of copper contamination only physical and chemical parameters are of primary interest, microbiological characteristics are not investigated.

Two phases of sampling campaign were undertaken in the Ramna and the Dhanmondi lakes. During the first campaign, starting from April, 1996 samples were collected from both the lakes. The second sampling campaign was carried out in January, 1997. During this second sampling campaign, water as well as sediment samples were collected from pre-selected points in both of these lakes. In this study,

- i) Dry period is considered to cover the end of spring to the end of summer (April and May) with some rainfall for almost three or four months.
- ii) Wet period covered the monsoon (June-July) with heavy rainfall, and
- iii) Interim period covered the summer (August-January) with less rainfall.

### **3.3 SAMPLING METHOD**

Water sample collection: Plastic containers were used to collect water samples during the sampling campaign. The containers were washed with dilute nitric acid and dried before water collection. At each sampling site, two liters of water sample were collected. In-situ temperature and pH of the sample at that location was also recorded. Temperature was measured with alcohol thermometer and pH was measured by digital pH-meter. The close-mouthed plastic bottles were submerged to mid depth at each location and opened, after filling the bottle it was capped and brought back to the surface.

In this study, water samples collected from mid depths at all sampling locations were considered to be representative of that location. For non-flowing lakes like Ramna and Dhanmondi lake, various chemical constituents in a water column can be considered to be in equilibrium at any location. However, speciation and distribution of chemical constituents in water close to the bottom sediment may, to some extent, differ from the water at the surface of the lake. Considering time and financial constrains, it was decided that water sample would be collected from mid depth at all locations.

Bed sediment collection: Two sampling sites in Ramna lake (locations 1&3) and three sampling sites in Dhanmondi lake (locations 1,2&5) were chosen for this purpose. Sediment sample from bed is collected with the help of 1ft hollow tube sampler prepared at the environmental engineering laboratory. The sampler is driven into sediment bed upto 1ft depth. The pipe is then pulled out in a way that sediment trapped into it remains within the pipe. The sediment sample along with the sampler was air dried in the laboratory. After 3/4 days when the sediment sample became hard, the soil column is taken out from the pipe. Two distinctly different colors were observed in each sediment sample indicating new layer. The columns were cut along the line of separation of two different colors. Depth of each soil sample, having different texture, was then measured. It was observed that upper layer of the sediment column was darker than the bottom layer. Sediment column of each layer is then grinded softly into their smallest natural particle/grain size by pressing with finger. The grain size distribution curves for each sediment was developed following sieve analysis.

### **3.4 PRESERVATION, STORAGE, PREPARATION AND ANALYSIS OF SAMPLES**

Sample preservation is difficult because almost all preservatives interfere with some of the tests. Some determinations are more likely to be affected than others by the duration of sample storage before analysis. Certain constituents are subjected to loss by adsorption on the sides of glass container walls. So, polethene bottles are preferred for storage of

samples for analysis of metal ions as these bottles are less likely to contaminate the sample than glass bottles.

Immediate analysis is ideal for reliable results. Storage at low temperature (4° C) is perhaps the best way to preserve most samples until the next day. Sample preservation techniques were followed as closely as possible to that of standard procedure of preservation.

Analysis of non-metallic components in water include determination of chloride, sulfate, pH, alkalinity, hardness, ammonium, nitrate, phosphate, total solids, suspended solids. pH was determined at the sampling locations using digital pH meter. Total solids, suspended solids, alkalinity, chloride and sulfate contents were determined by volumetric methods according to the procedure specified in Standard Methods (Standard Methods, 1985). Ammonium, nitrate and phosphate were determined by using a visible ultraviolet spectrophotometer (HACK, Model no. DR/EL4).

Water as well as sediment samples were tested for total copper concentrations. Analysis of metal ions in water and sediment samples were performed by an Atomic Adsorption Spectrophotometer (Shimadzu Corporation, Model no. AAS 680).

Before analyzing the samples for metal concentration, AAS was calibrated with standard solution of that specific metal. Water and sediment samples are digested in order to convert all the metallic forms into ionic state. For digesting water samples nitric acid (1:3) and hydrochloric acid (1:3) were mixed in a ratio one to three and was then added to 100ml of water sample. Then it was boiled for about 5 to 10 minutes and the volume was reduced to about half. When the boiled samples cooled to room temperature, they were adjusted to 100ml with distilled water and were then filtered. The filtered acidic solutions were then ready for analysis using AAS.

To digest sediment samples of each grain size, 100 ml nitric acid and 30 ml hydrochloric acid were mixed with about 10 mg of oven dried sediment sample. Then about 100 ml of

distilled water was added to the sample and the mixture was boiled for 15 to 20 minutes. The sample was then allowed to cool for about 30 minutes and substantially adjusted to 500 ml followed by thorough stirring and filtering. The filtered sample was then analyzed by AAS. The metal content of the sediment sample in mg/kg of dry weigh or in ppm is then calculated by,

$$M = C \times L / W \times 10^3 \text{ -----(3.1)}$$

where

M = Metal concentration in mg/kg (ppm)

C = Metal concentration in mg/l found by AAS

L = Volume of sample in liter ( 0.5 liter in this case )

W = Mass of sediment in gm (10 gm in this case )

### **3.5 COLLECTION, PREPARATION, AND ANALYSIS OF FISH SAMPLES**

Heavy metal deposited in the sediment column as well as those persisting in the water column in large quantities are readily available to aquatic biota. Specially, the bottom feeding fish are more likely to accumulate in different parts of the body.

In order to investigate the bioavailability of copper in the Dhanmondi lake a bottom feeding fish sample namely, Nilotika, was collected. Due to lack of any specific literature for extraction of heavy metal from fish tissues, an approach similar to that of extraction of heavy metal from sediment was used. However, instead of per unit of dry mass the concentration per unit wet mass of various parts of Nilotika fish was determined.

Various parts of the fish (e.g. gills, muscle, skin, stomach, external bones and head muscles) were first separated and weighed. To digest these parts, 25 ml of HNO<sub>3</sub> and 50 ml of HCl were mixed with each separated parts. Then about 250 ml of water was added to each samples and each was boiled for about 15 to 30 minutes followed by slow cooling. Boiling of the samples was done carefully, because, boiled water may spill off from the beaker and cause accident and errorious result. The volume of each cooled



samples was measured before filtering. Copper concentration in the filtered samples was measured by Atomic Adsorption Spectrometer. The metal contents of various parts of the fish in mg/kg (wet mass) were then determined by using Eqn. (3.1), with W bearing the wet mass of each part of the fish in gm.

### 3.6 PREPARATION AND STORAGE OF STANDARD COPPER SOLUTION

A standard metal solution of copper was prepared in the optimum concentration range by appropriate dilution of the stock metal solution. For dilution deionize water containing 1.5 ml conc.  $\text{HNO}_3$  /L was used.

### 3.7 VISIBLE AND ULTRAVIOLET SPECTROMETRY

Determination of low concentrations by visible ultraviolet spectrometer is based on Beer - Lambert law given by;

$$A = \epsilon cl$$

where,

A = absorbance of radiation at a particular wavelength; =  $\log ( I_0/I )$

$I_0$  = intensity of incident radiation;

I = intensity of transmitted radiation;

$\epsilon$  = proportionality constant ( molar absorptivity;  $1 \text{ mol}^{-1} \text{ cm}^{-1}$  ) ;

c = concentration of absorbing species ( mol/L )

l = path length of light beam (cm)

The instrument used to measure the absorption of light can range from sophisticated laboratory instruments, which can operate over the whole visible-ultraviolet range to portable colorimeters using natural visible light, which are used as a field instrument.

This makes absorption spectrometry one of the most useful and versatile technique to an environmental analyst.

None of the common ions in water absorb light in the visible region of the spectrum (natural water is usually colorless). The technique involves the production of light absorbing derivatives of these ions. This can be performed for almost all the common ions (except sulfate) and also ammonia. Chloride, fluoride, nitrate, nitrite, and phosphate can be analyzed after formation of derivatives.

As an example of the technique, the procedure for phosphate involves the addition of a mixed reagent (sulfuric acid, ammonium molybdate, ascorbic acid, antimony potassium titrate) to a known volume of sample, diluting to volume, shaking and leaving for 10 min. A blue phosphomolybdenum complex is produced, the absorbance of which is measured. The concentration is calculated using a predetermined calibration graph derived from standard solutions treated in the same way. Similar procedure can be followed for other anions, with different set of reagents for different anions.

### **3.8 Atomic absorption spectrometry (AAS)**

In this method, a light beam of correct wavelength for a particular metal is directed through a flame. The flame atomizes the sample, producing atoms in their ground (lowest) electronic energy state. These are capable of absorbing radiation from the lamp.

Although the equipment appears completely different from other forms of adsorption spectrometry, the law by which absorption of light is related to concentration is similar to that used for absorption of visible and ultraviolet radiation, which is the Beer-Lambert law. The concentration range over which the law applies for Atomic Adsorption Spectrometry (AAS) is usually 0-5 mg/l. In this study, AAS has been primarily used for analysis of metal ions.

Atomic absorption is indeed sensitive and, if it is used for more common ions, the water samples would have to be diluted before analysis. Calcium and magnesium are analyzed by flame AAS, often after sample dilution. If the technique is used for sodium and potassium analysis, lower sensitivity absorption lines, rather than higher sensitivity lines, would be used in addition to diluting the sample. Atomic emission (flame photometry) is, however, the preferred technique of these ions.

## **CHAPTER - 4**

### **DATA ANALYSIS AND RESULTS**

#### **4.1 STATUS OF WATER OF DHANMONDI AND RAMNA LAKES**

Reservoirs and lakes receiving domestic and industrial pollutants, storm sewer discharges through different inlets are susceptible to heavy metal contamination. Dhanmondi and Ramna lake, located at the heart of the city, receive considerable amount of pollutants from these sources. Both of these lakes are widely used for bathing, swimming, fishing and other recreational purpose. Copper contamination is, therefore, a major concern for both Dhanmondi and Ramna lake especially because of the fact that these lakes have very little scope of self purification.

Heavy metals, such as copper, are usually present in natural water in various forms, e.g. as free ion, as complexes with organic and inorganic legands, or in sorbed state. All the chemical forms of a specific heavy metal are not toxic to aquatic biomass or human. In reality, only a few of these are toxic when threshold concentrations are exceeded. The chemical forms in which copper would exist in Ramna and Dhanmondi lake depend on chemical composition of water, e.g., pH, presence of organic and inorganic legands, and adsorbents. Thus characterization of the lake water in as much detail as possible is essential to evaluate copper contamination. To achieve that objective the spatial and seasonal variations various chemical constituents in Dhanmondi and Ramna Lake have been studied extensively. A detailed description of the same is given in the following sections.

##### **4.1.1 Spatial and Seasonal Variation of Copper in Dhanmondi and Ramna Lakes**

The average total concentration of copper in the water and adsorbed on suspended sediment of both the lakes are shown in Fig 4.1 and fig 4.2. Table 4.1 and Table 4.2 show the numerical values of these analysis. It is evident that copper concentrations in water



during a particular season does not vary significantly and remain more or less uniform during dry period as well as wet period. There is a slight variation of concentration of copper at the sampling locations in the intermediate period. Overall, it can be said that concentration of copper in water is uniform throughout the lake. However, concentration of copper in lake water during dry season is slightly higher than those in other seasons. Dilution, caused by increased inflow of rain water and surface run-off during wet season, may have caused a decrease in total copper concentration. In the intermediate period, at the advent of winter season these concentrations seem to follow an increasing trend.

The aqueous copper concentration have been found to vary between 0.186 to 0.21 mg/l in the dry period, from 0.102 to 0.153 mg/l in wet period and from 0.096 to 0.192 mg/l in intermediate period in Dhanmondi lake. The same for Ramna lake have been found to vary between 0.127 to 0.203 mg/l in dry period, 0.07 to 0.165 mg/l in wet period and 0.104 to 0.33 mg/l in intermediate period. Variation of aqueous copper concentration in the samples collected in different times during a particular period may be attributed to variations in daily input of copper, sampling and in some cases analytical errors.

Fig 4.1 and Fig 4.2 also shown average concentration of copper in adsorbed to the suspended solids at the seven sampling locations of Dhanmondi lake and four sampling locations of Ramna lake during three different periods of the year. Compared to aqueous copper concentration these are relatively low. Suspended solids consist of hydrous metal oxides and colloidal organic sorbents usually sorb metal ions causing an increase in the adsorbed portion in the sediment. Concentration of copper (any metal ion) on suspended solid is also dependent on pH, with higher pH promoting sorption.

Seasonal variations of copper adsorbed on suspended solids, do not show any clear trend. Adsorbed copper concentrations during dry period ranges from 0.02 to 0.153 mg/l, from 0.06 to 0.11 mg/l in wet period and 0.013 to 0.063 mg/l in intermediate period for Dhanmondi lake. In case of Ramna lake copper concentration in dry period varies from 0.013 to 0.038 mg/l, from 0.006 to 0.025 mg/l in wet period and 0.025 to 0.184 mg/l in interim period.



Table 4.1 : Copper concentration (mg/l) of water at different locations in Dhanmondi Lake

| Sl. No. | Date    | Point 1 (mg/l) |       | Point 2 (mg/l) |       | Point 3 (mg/l) |       | Point 4 (mg/l) |       | Point 5 (mg/l) |       | Point 6 (mg/l) |       | Point 7 (mg/l) |       |
|---------|---------|----------------|-------|----------------|-------|----------------|-------|----------------|-------|----------------|-------|----------------|-------|----------------|-------|
|         |         | UF             | F     | UF             | F     | UF             | F     | UF             | F     | UF             | F     | UF             | F     | UF             | F     |
| 1       | 4-4-96  | .7028          | .1044 | .3076          | .2253 | .3077          | .2049 | .2649          | .1930 | .2631          | .2295 | .3079          | .2792 | .3167          | .2913 |
| 2       | 12-4-96 | .2472          | .2267 | .2394          | .2230 | .2437          | .1787 | .2469          | .2246 | .2645          | .2528 | .1921          | .1783 | .3171          | .2079 |
| 3       | 15-5-96 | .2327          | .1839 | .4663          | .1623 | .2613          | .2029 | .1919          | .1419 | .2206          | .1166 | .2936          | .2460 | .3844          | .1844 |
| 4       | 17-5-96 | .2725          | .2135 | .230           | .2116 | .2360          | .1809 | .2734          | .2566 | .2323          | .1879 | .1453          | .1419 | .257           | .1773 |
| 5       | 31-5-96 | .2629          | .2260 | .2060          | .1652 | .2298          | .1604 | .1690          | .1622 | .2540          | .2493 | .2037          | .1993 | .2732          | .1356 |
| 6       | 4-6-96  | .1355          | .1139 | .2334          | .0967 | .1428          | .0868 | .1679          | .0941 | .1509          | .1111 | .2014          | .1266 | .1756          | .062  |
| 7       | 7-6-96  | .2826          | .1883 | .2067          | .1984 | .1847          | .1281 | .1980          | .1354 | .2544          | .1183 | .2087          | .1319 | .2514          | .1441 |
| 8       | 27-1-96 | .184           | .153  | .213           | .192  | .190           | .137  | .153           | .128  | .126           | .096  | .144           | .131  | .219           | .155  |

Table 4.2 : Copper concentration (mg/l) of water at different locations in Ramna Lake

| SL NO. | DATE    | POINT 1 |       | POINT 2 |       | POINT 3 |       | POINT 4 |       |
|--------|---------|---------|-------|---------|-------|---------|-------|---------|-------|
|        |         | NF      | F     | NF      | F     | NF      | F     | NF      | F     |
| 1      | 4-4-96  | .2197   | .1821 | .21     | .1868 | .1699   | .1269 | .2172   | .2047 |
| 2      | 16-6-96 | .0767   | .0723 | .1803   | .1667 | .1552   | .1260 | .1228   | .1057 |
| 3      | 27-1-97 | .201    | .116  | .174    | .14   | .285    | .102  | .356    | .332  |

# DHANMONDI LAKE

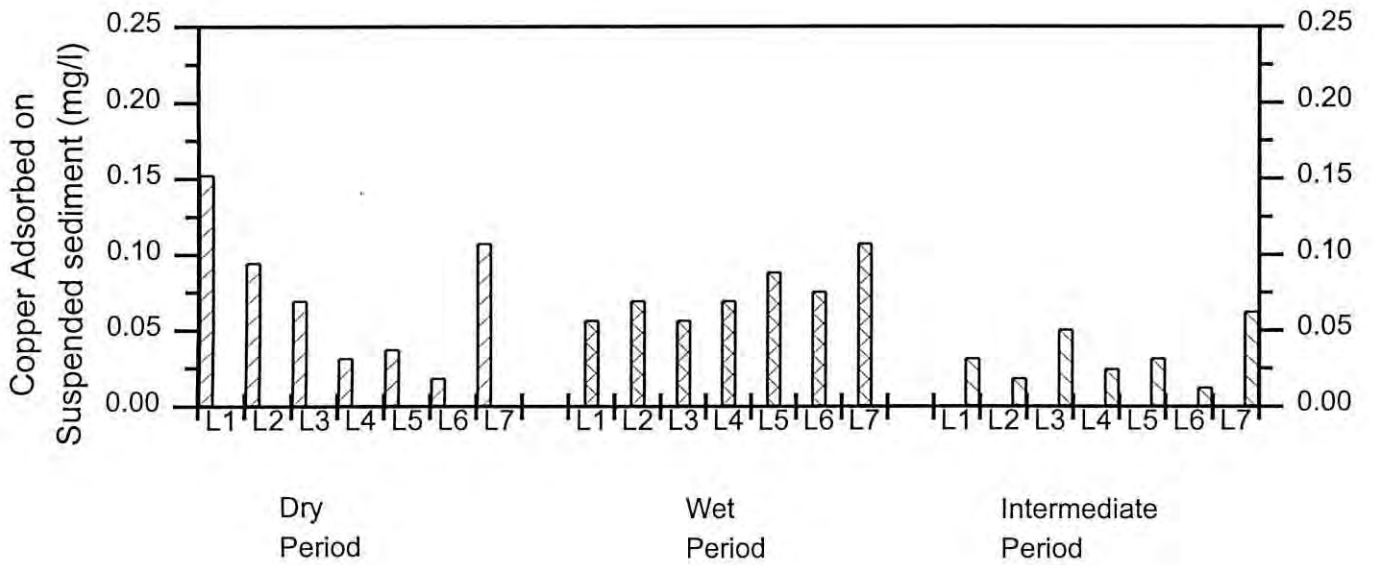
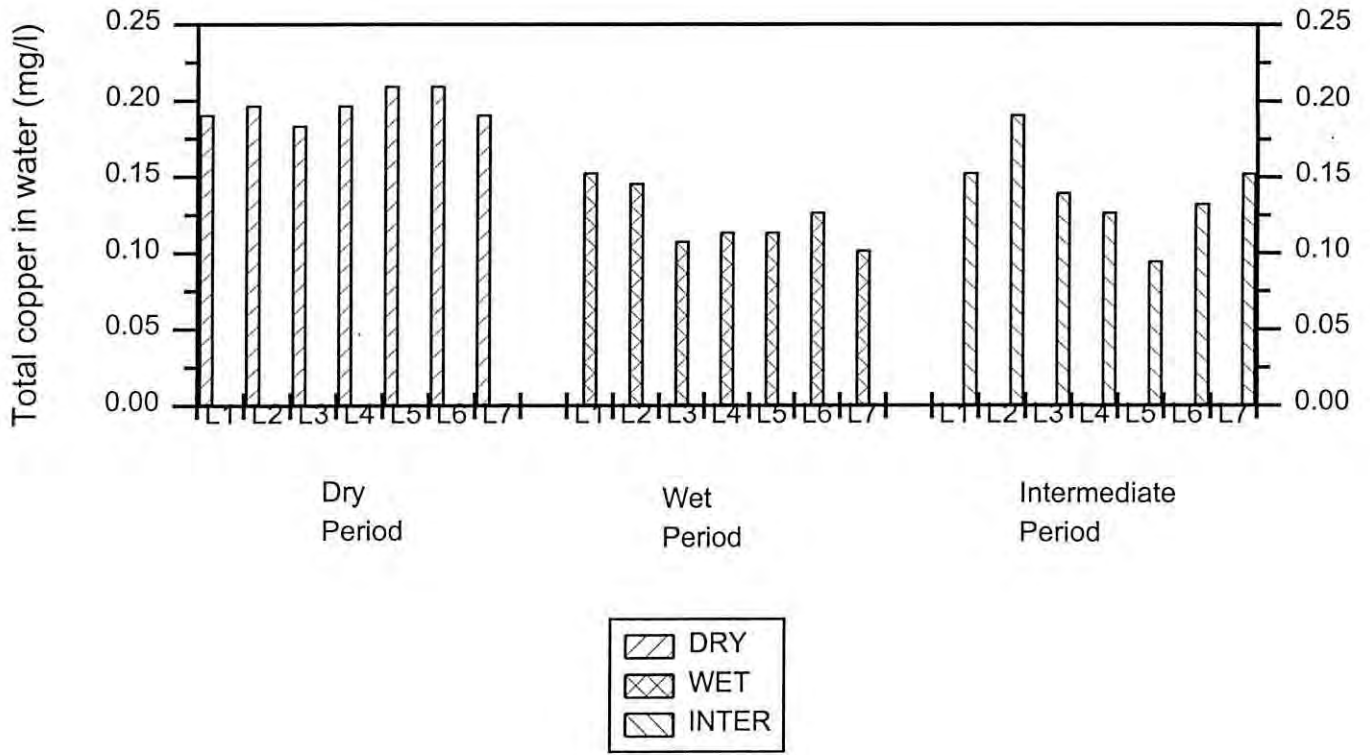


Fig. 4.1: Average concentration of copper at the sampling locations

## RAMNA LAKE

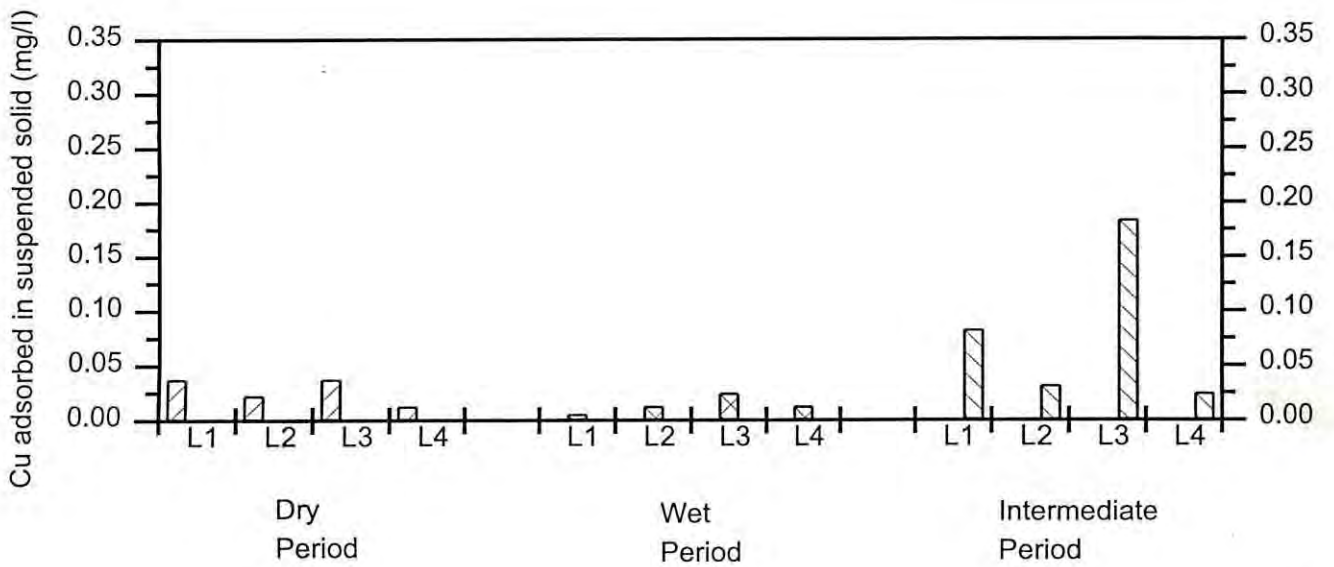
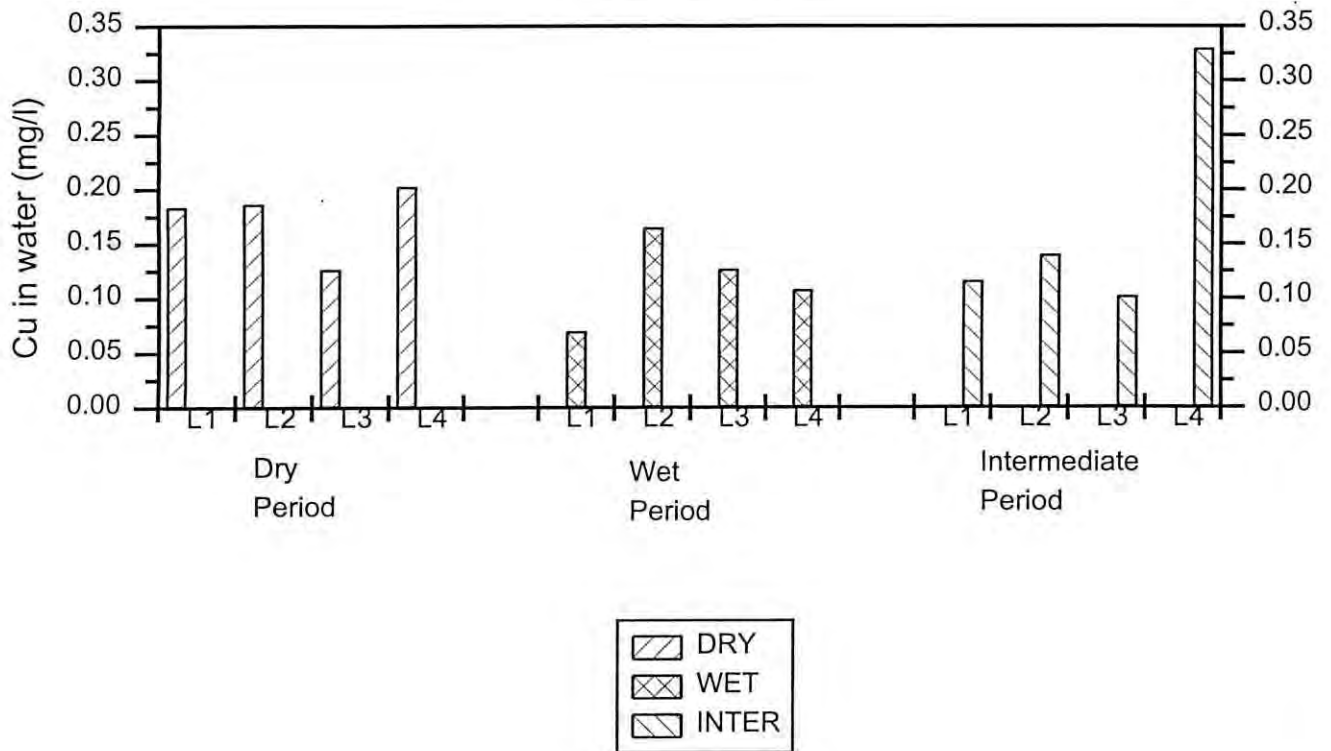


Fig. 4.2 : Average concentration of copper at the sampling location

Other cations such as calcium, magnesium, potassium, sodium were also measured for Dhanmondi lake and are given in table of Appendix A. However, due to instrumental malfunction these cations could not be measured for the Ramna Lake.

#### 4.1.2 Variation of pH and Temperature

Tab. 4.3 and Fig. 4.3, Fig. 4.4 show variation of pH in lake water at seven sampling locations of Dhanmondi Lake. Fig 4.5 shows the variation of pH at lake water at four sampling locations of Ramna Lake. Average pH of lake water in Dhanmondi lake varies from 6.9 to 8.5 during dry period. In the wet period it varies from 7.3 to 8.5 and in interim period it varies from 7.2 to 8.7. In Ramna lake pH varies from 7.0 to 8.9 during dry period, 7.3 to 8.0 during wet period and 7.1 to 7.5 during interim period. Thus it is apparent that the variation of pH throughout the year in these two lakes is insignificant indicating a well buffered system. But water of both lakes remain slightly alkaline throughout the year. pH found during the first sampling campaign was little bit higher than other periods for both these lakes and pH of dry period is slightly higher than the wet and intermediate period. High value of pH of the lake water facilitates adsorption and subsequent sedimentation of copper resulting in accumulation in bed sediment. Although a number of sampling points are located close to the pollutant inlets (locations 1,2,3,7 of Dhanmondi lake and location 1 of Ramna lake) and some locations of are covered with water hyacinth and trees, no significant spatial variation of pH was observed.

Tab. 4.4 and Fig. 4.6, Fig. 4.7 show the variation of temperature of Dhanmondi lake. Fig. 4.8 shows temperature of Ramna lake at sampling locations. It was observed that temperature of the lake water varies throughout the year. At the beginning of dry period temperature was found to be less than 30<sup>0</sup> C which increased with time. The maximum temperature was recorded in the month of May and June i.e. at the end of dry period and in wet period. Then temperature decreased below 25<sup>0</sup> C during intermediate period (winter).

In Ramna lake at all locations temperature was higher in dry period. It decreased during wet period and temperature was lowest during intermediate period. Spatial variation of



Table 4.3: Variation of pH at different periods at the sampling locations.

| DHANMONDI LAKE |         |      |     |     |     |     |     |     |
|----------------|---------|------|-----|-----|-----|-----|-----|-----|
| Sampling       | Date    | P-1  | P-2 | P-3 | P-4 | P-5 | P-6 | P-7 |
| 1              | 4-4-96  | 8.4  | 8.5 | 8.4 | 8.4 | 8.4 | 8.4 | 8.4 |
| 2              | 12-4-96 | 6.9  | 7.1 | 7.0 | 7.0 | 7.0 | 7.1 | 7.1 |
| 3              | 15-5-96 | 7.9  | 7.4 | 7.5 | 7.4 | 8.4 | 7.6 | 8.1 |
| 4              | 17-5-96 | 7.88 | 7.7 | 7.5 | 8.0 | 8.2 | 7.8 | 7.9 |
| 5              | 31-5-96 | 7.3  | 8.3 | 8.2 | 7.9 | 7.4 | 8.1 | 8.2 |
| 6              | 4-6-96  | 7.7  | 7.5 | 7.4 | 7.4 | 7.5 | 7.4 | 7.5 |
| 7              | 7-6-96  | 7.8  | 7.3 | 7.6 | 7.4 | 8.5 | 7.8 | 8.3 |
| 8              | 27-1-97 | 7.8  | 7.2 | 7.3 | 8.7 | 8.1 | 7.3 | 8.3 |
| RAMNA LAKE     |         |      |     |     |     |     |     |     |
| Sampling       | Date    | P-1  | P-2 | P-3 | P-4 |     |     |     |
| 1              | 24-5-96 | 8.7  | 8.9 | 7.0 | 8.9 |     |     |     |
| 2              | 16-6-96 | 7.3  | 7.4 | 8.0 | 7.5 |     |     |     |
| 3              | 27-1-97 | 7.1  | 7.5 | 7.5 | 7.4 |     |     |     |

Table 4.4: Variation of Temperature ( $^{\circ}\text{C}$ ) at different periods at the sampling locations

| DHANMONDI LAKE |         |      |      |      |      |      |     |      |
|----------------|---------|------|------|------|------|------|-----|------|
| Sampling       | Date    | P-1  | P-2  | P-3  | P-4  | P-5  | P-6 | P-7  |
| 1              | 4-4-96  | 29   | 28   | 29   | 28   | 29   | 29  | 29   |
| 2              | 12-4-96 | 31   | 31   | 31   | 31   | 30   | 31  | 31   |
| 3              | 15-5-96 | 32   | 31.5 | 32   | 30.5 | 34.5 | 32  | 32.5 |
| 4              | 17-5-96 | 32.5 | 32.5 | 31.5 | 32.5 | 33   | 32  | 32   |
| 5              | 31-5-96 | 32   | 32   | 32.5 | 32.5 | 31.5 | 32  | 32   |
| 6              | 4-6-96  | 30   | 30   | 29   | 28.5 | 29   | 29  | 29   |
| 7              | 7-6-96  | 32.5 | 32   | 31.5 | 30.5 | 32   | 32  | 32   |
| 8              | 27-1-97 | 20.5 | 19   | 19.5 | 20.5 | 19.5 | 20  | 20   |
| RAMNA LAKE     |         |      |      |      |      |      |     |      |
| Sampling       | Date    | P-1  | P-2  | P-3  | P-4  |      |     |      |
| 1              | 24-5-96 | 35   | 34.5 | 35   | 34.5 |      |     |      |
| 2              | 16-6-96 | 33   | 33.5 | 33.5 | 33   |      |     |      |
| 3              | 27-1-97 | 21   | 20   | 20   | 20   |      |     |      |



# DHANMONDI LAKE

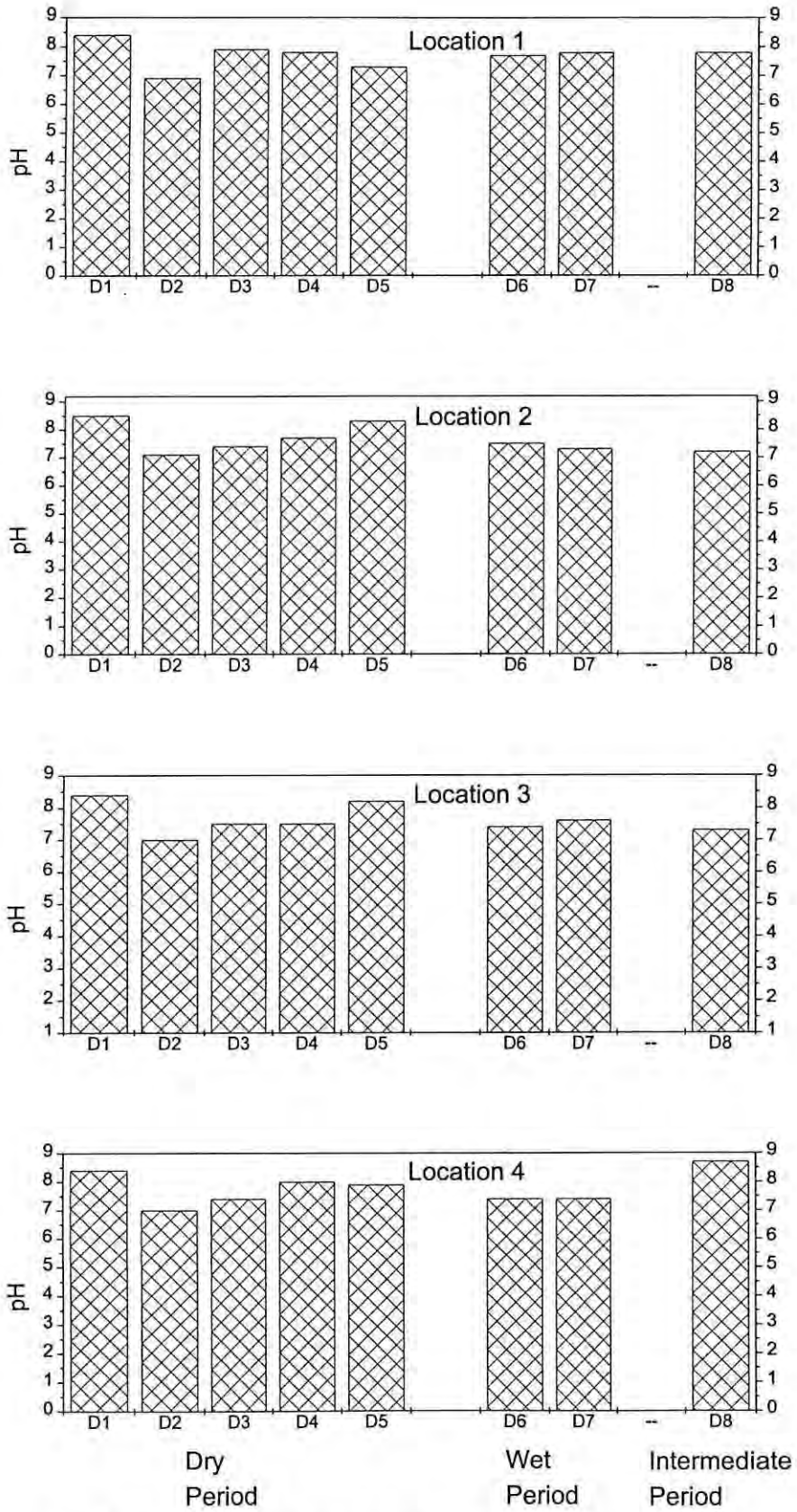


Fig. 4.3 : Seasonal variation of pH at the sampling locations

# DHANMONDI LAKE

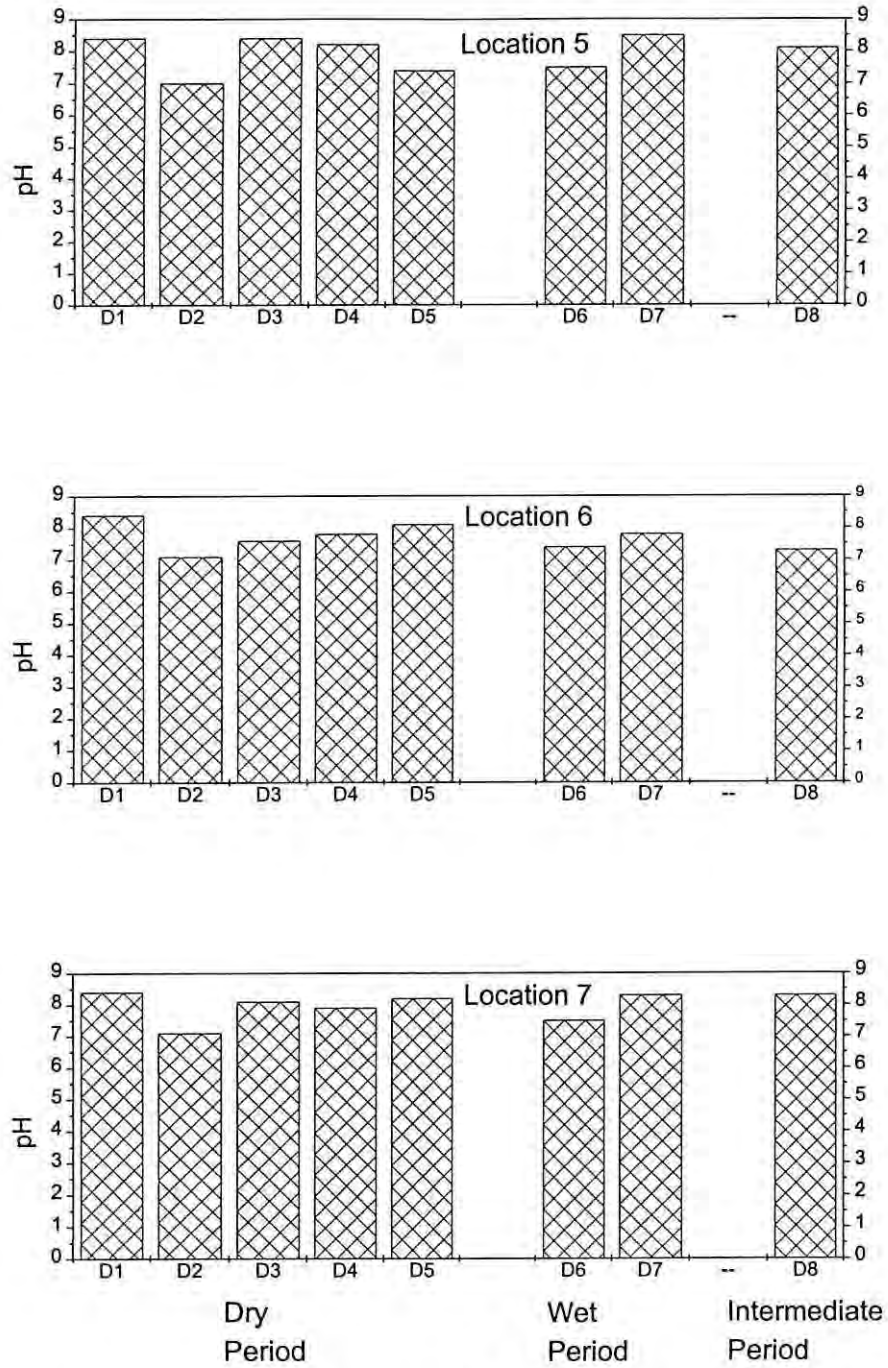


Fig. 4.4 : Seasonal variation of pH at the sampling locations

# RAMNA LAKE

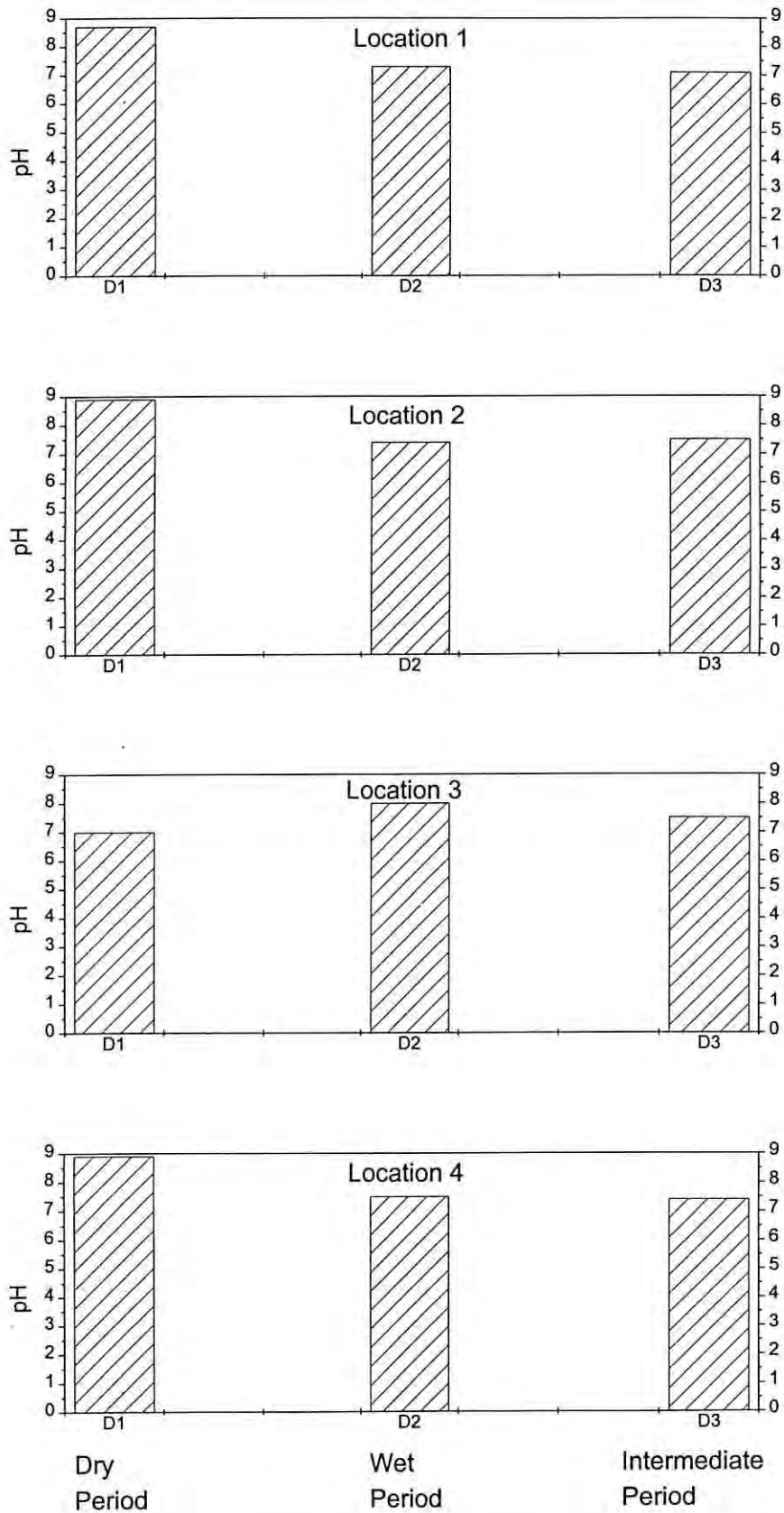


Fig. 4.5 :Seasonal variation of pH at the sampling locations

# DHANMONDI LAKE

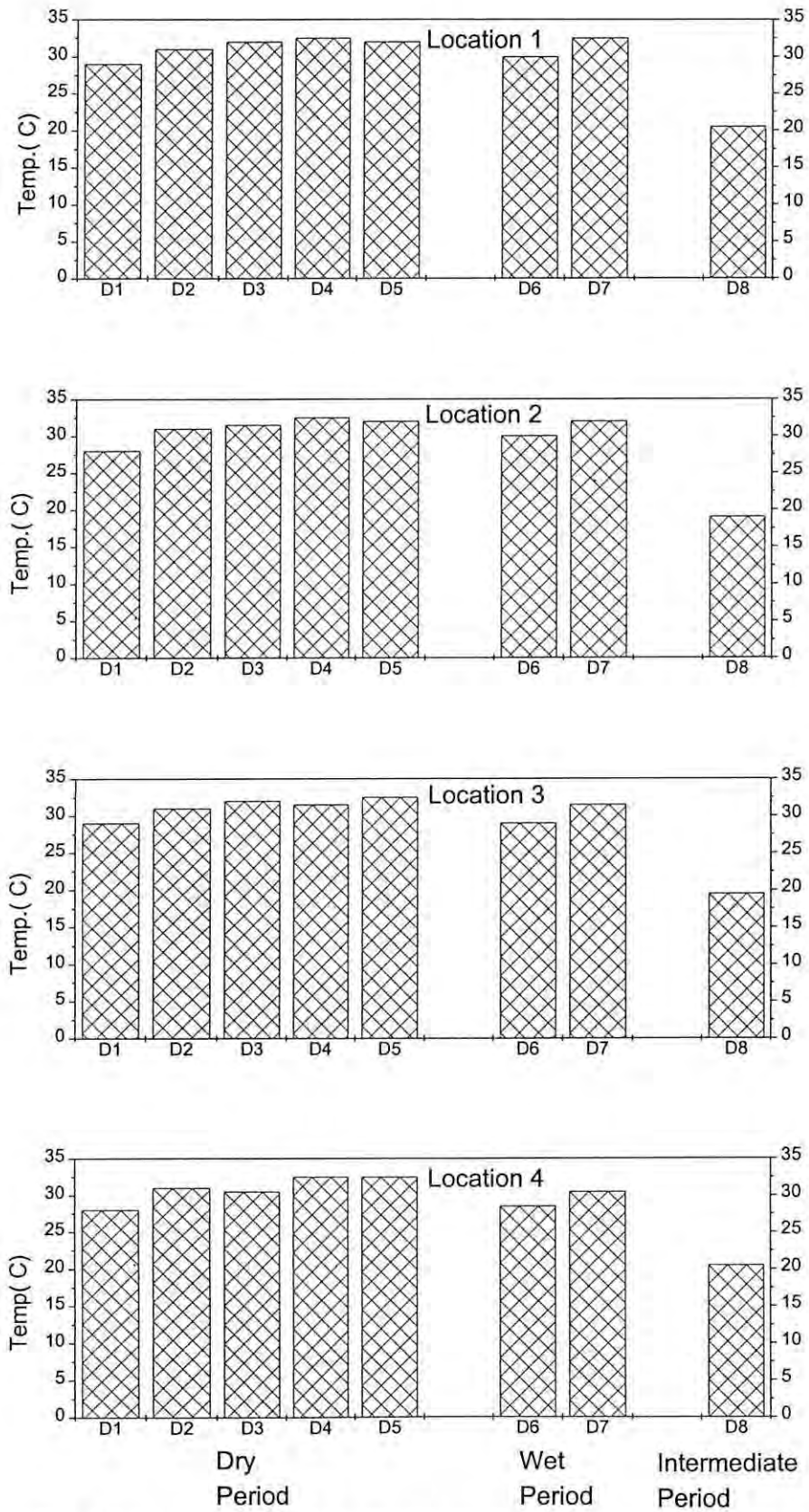


Fig. 4.6 :Seasonal variation of temperature at the sampling locations



## DHANMONDI LAKE

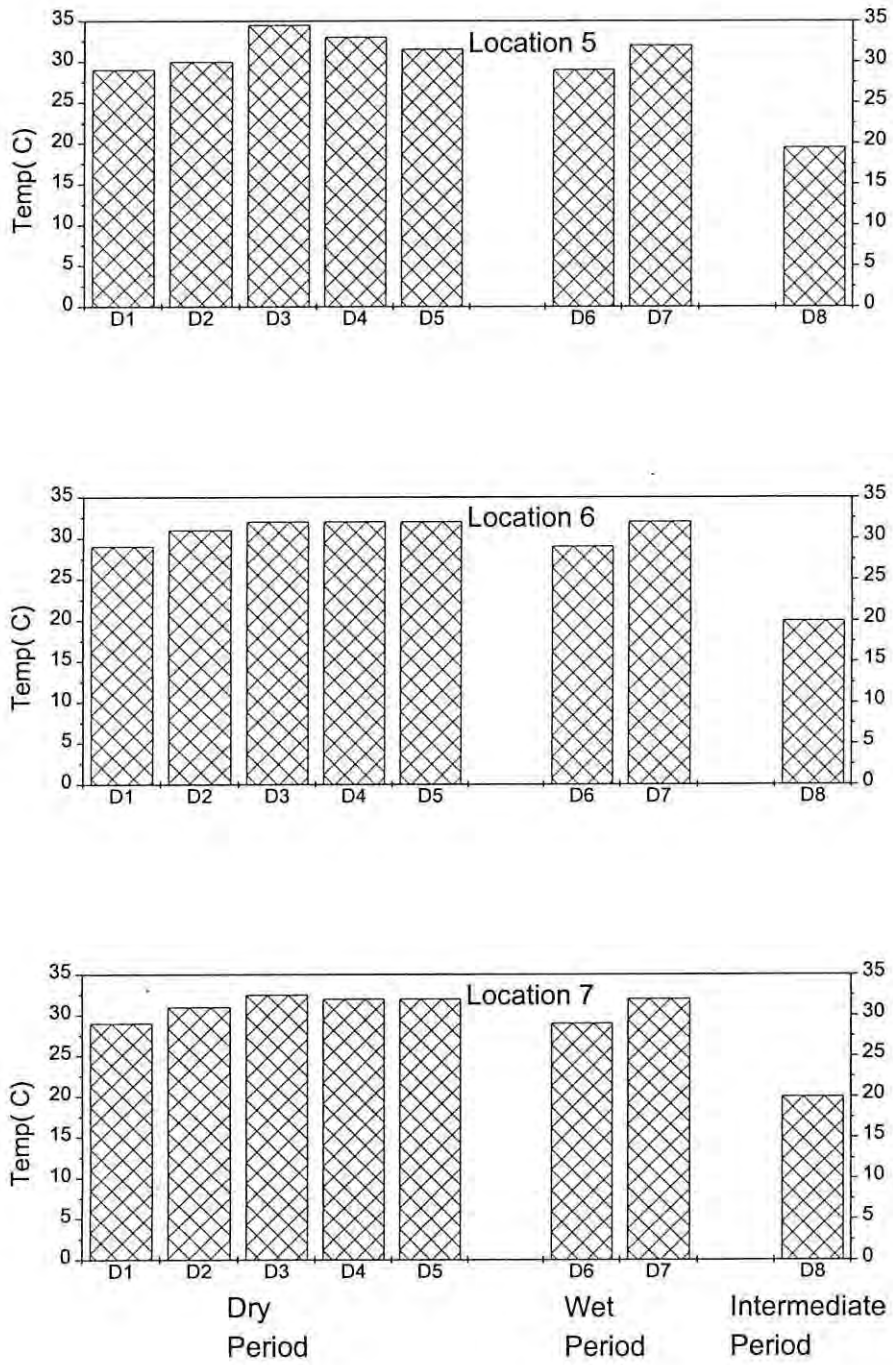


Fig. 4.7 : Seasonal variation of temperature at the sampling locations

# RAMNA LAKE

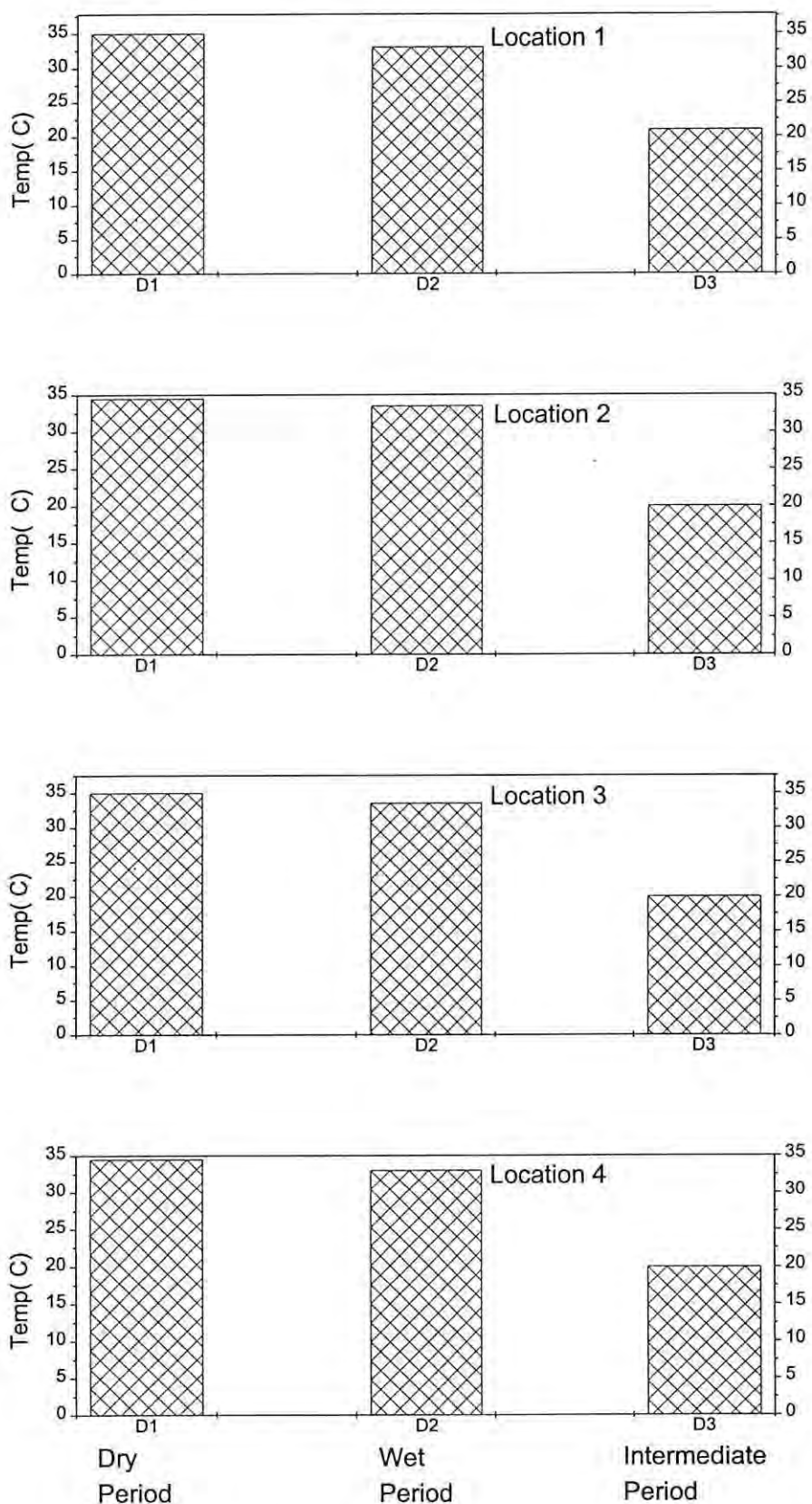


Fig.4.8 : Seasonal variation of temperature at the sampling locations

temperature was observed in dry period (1°C to 6.5°C) but temperature do not vary significantly for other locations in other periods.

#### 4.1.3 Variation of Alkalinity and Chloride

Variation of alkalinity at all sampling points of Dhanmondi lake are shown in Tab 4.5, Fig 4.9 to Fig. 4.10. That of alkalinity at all the sampling locations of Ramna lake are shown in Fig. 4.11. Distribution of chloride in Dhanmondi lake at all sampling locations are shown in Fig. 4.12 to Fig. 4.13 and Fig. 4.14 shows the same at Ramna lake. Tab. 4.6 shows the numerical values of these analysis.

It can be observed that in both of these lakes, alkalinity is high in dry period and it decreases in wet period and begin to increase again at the onset of intermediate period (winter). The decrease of alkalinity during wet period may be attributed to dilution effect during the wet season resulting from rainfall and surface run off. In Dhanmondi lake, during dry period, alkalinity ranges from 45 mg/l to as high as 160 mg/l; in wet period alkalinity ranges between 34 mg/l to 120 mg/l. In the interim period alkalinity again increases which ranges from 123 mg/l to 144 mg/l. In Ramna lake alkalinity in dry period ranges from 95 mg/l to 114 mg/l; in wet period 85 mg/l to 99 mg/l and in intermediate period 98 mg/l to 111 mg/l. Similar trend is also observed in case of chloride concentrations. Chloride concentration in all sampling locations of Dhanmondi lake during dry period ranged from 45 mg/l to 180 mg/l. During wet period concentration of chloride is within 34 mg/l to 58 mg/l and in interim period it is from 55 mg/l to 63 mg/l. In Ramna lake concentration of chloride in dry period ranges from 37 mg/l to 48 mg/l, in wet period 23 mg/l to 32 mg/l and in interim period 30 mg/l to 43 mg/l. Slightly elevated level of chloride were found in the southern part of the lake (particularly at location 1,3,6). Elevated chloride concentration indicate sewage pollution in Dhanmondi lake may be caused by discharge of sewage through inlet points in the southern part of the lake. Since carbonate, bicarbonate, chloride form complexes with copper presence of these species are likely to influence speciation of copper.

Table 4.5: Variation of alkanity at different periods at the sampling locations :

| DHANMONDI LAKE |         |     |     |     |     |     |     |     |
|----------------|---------|-----|-----|-----|-----|-----|-----|-----|
| Sampling       | Date    | P-1 | P-2 | P-3 | P-4 | P-5 | P-6 | P-7 |
| 1              | 4-4-96  | 146 | 140 | 152 | 125 | 160 | 150 | 115 |
| 2              | 12-4-96 | 140 | 142 | 142 | 120 | 144 | 138 | 125 |
| 3              | 15-5-96 | 128 | 126 | 124 | 95  | 136 | 122 | 90  |
| 4              | 17-5-96 | 126 | 120 | 118 | 90  | 124 | 116 | 90  |
| 5              | 31-5-96 | 118 | 114 | 114 | 45  | 122 | 114 | 50  |
| 6              | 4-6-96  | 106 | 106 | 106 | 50  | 120 | 108 | 48  |
| 7              | 7-6-96  | 90  | 74  | 72  | 37  | 95  | 87  | 34  |
| 8              | 27-1-97 | 137 | 137 | 125 | 126 | 126 | 123 | 144 |
| RAMNA LAKE     |         |     |     |     |     |     |     |     |
| Sampling       | Date    | P-1 | P-2 | P-3 | P-4 |     |     |     |
| 1              | 24-5-96 | 95  | 98  | 114 | 106 |     |     |     |
| 2              | 16-6-96 | 92  | 91  | 99  | 85  |     |     |     |
| 3              | 27-1-97 | 110 | 98  | 103 | 111 |     |     |     |

Table 4.6: Variation of Chloride (mg/l) at different periods at the sampling locations :

| DHANMONDI LAKE |         |     |      |     |     |     |     |     |
|----------------|---------|-----|------|-----|-----|-----|-----|-----|
| Sampling       | Date    | P-1 | P-2  | P-3 | P-4 | P-5 | P-6 | P-7 |
| 1              | 4-4-96  | 120 | 120  | 120 | 125 | 110 | 165 | 115 |
| 2              | 12-4-96 | 180 | 135  | 145 | 120 | 105 | 160 | 125 |
| 3              | 15-5-96 | 120 | 1.05 | 115 | 95  | 70  | 100 | 90  |
| 4              | 17-5-96 | 100 | 105  | 80  | 90  | 90  | 90  | 90  |
| 5              | 31-5-96 | 45  | 53   | 55  | 45  | 45  | 53  | 50  |
| 6              | 4-6-96  | 53  | 58   | 55  | 50  | 53  | 55  | 48  |
| 7              | 7-6-96  | 40  | 43   | 40  | 37  | 35  | 44  | 34  |
| 8              | 27-1-97 | 53  | 55   | 58  | 63  | 58  | 60  | 59  |
| RAMNA LAKE     |         |     |      |     |     |     |     |     |
| Sampling       | Date    | P-1 | P-2  | P-3 | P-4 |     |     |     |
| 1              | 24-5-96 | 48  |      | 38  | 37  |     |     |     |
| 2              | 16-6-96 | 23  | 25   | 24  | 32  |     |     |     |
| 3              | 27-1-97 | 43  | 34   | 30  | 30  |     |     |     |



## DHANMONDI LAKE

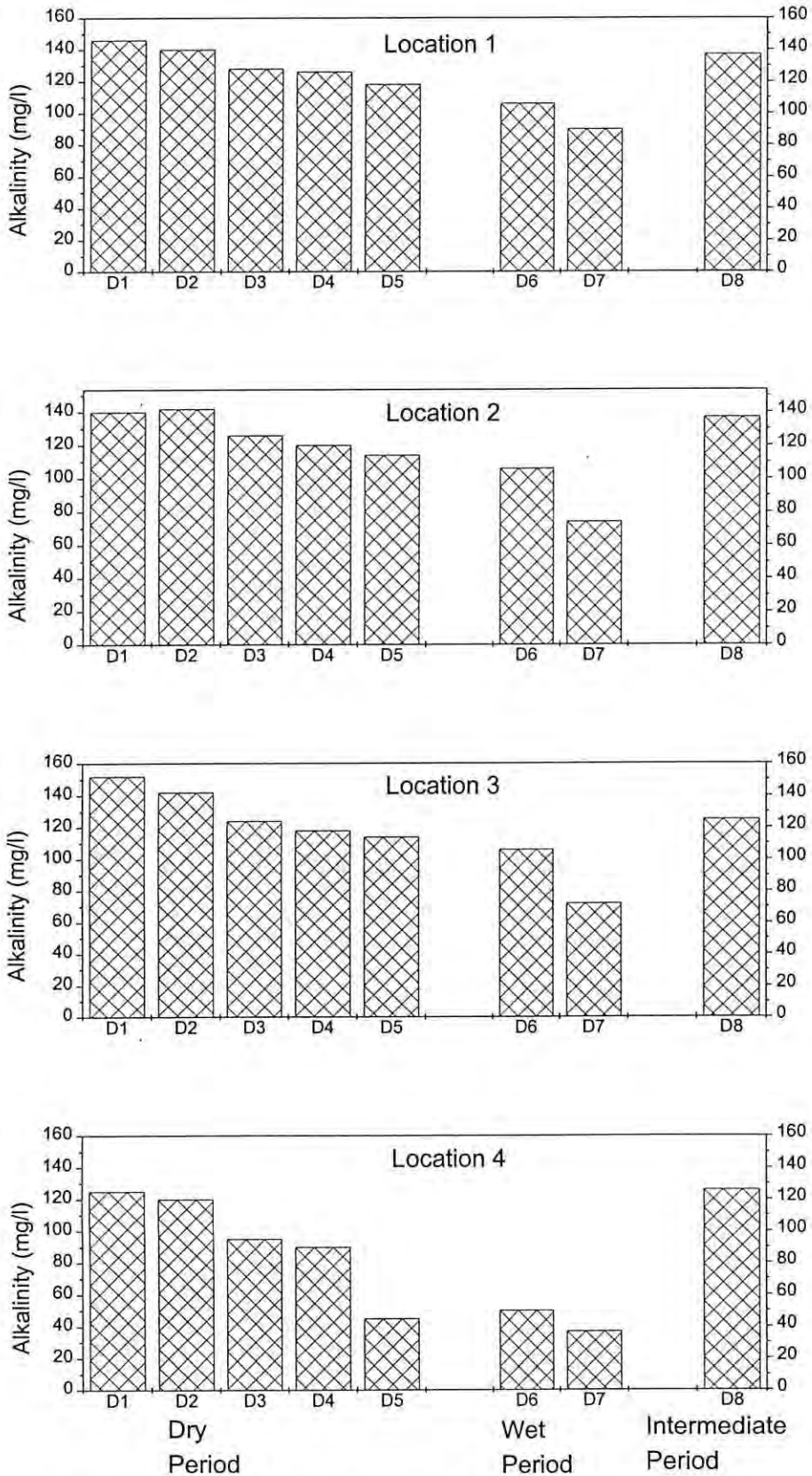


Fig.4.9 : Seasonal variation of alkalinity at sampling locations

# DHANMONDI LAKE

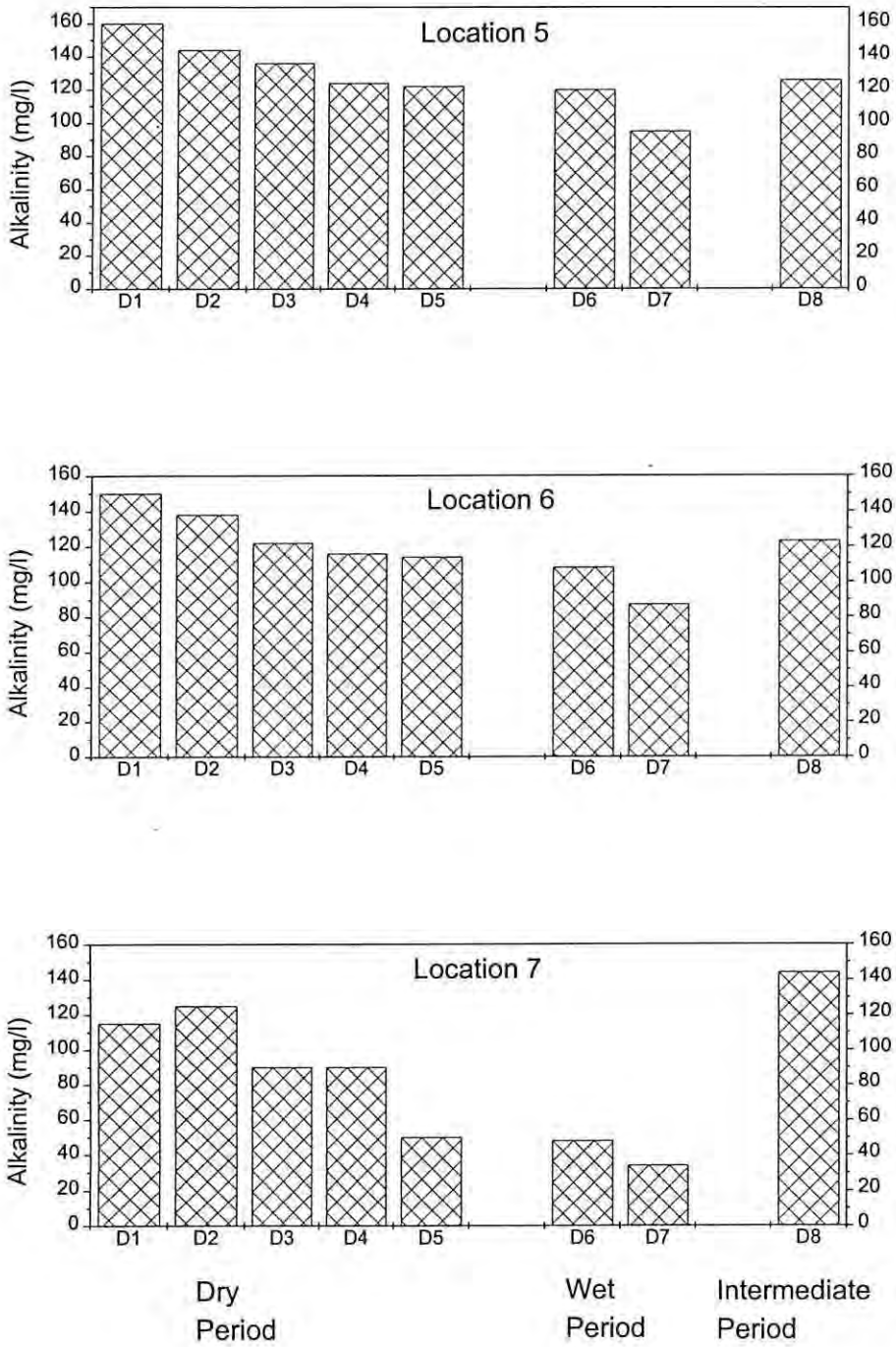


Fig. 4.10: Seasonal variation of alkalinity at sampling locations

# RAMNA LAKE

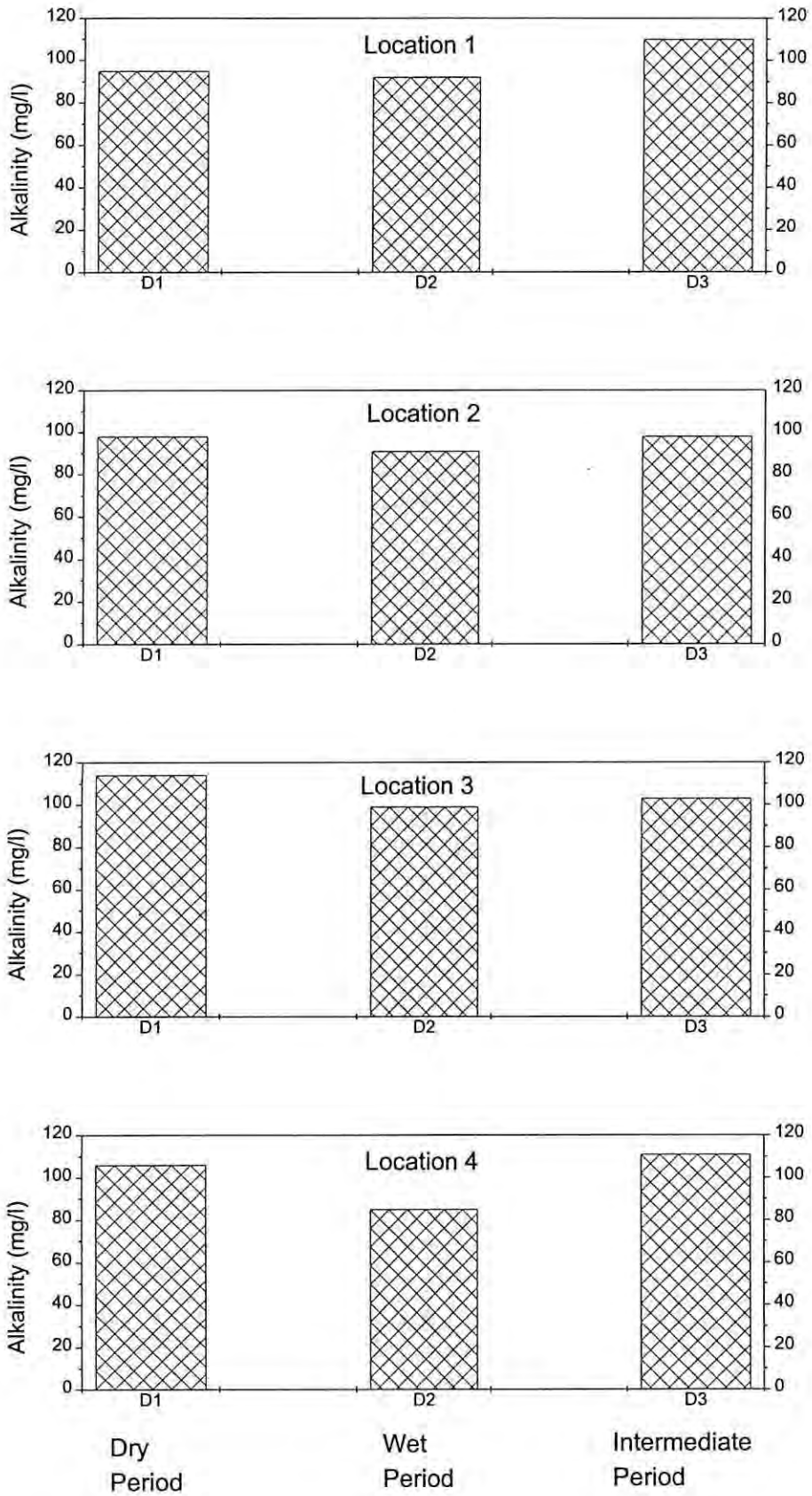


Fig.4.11: Seasonal variation of alkalinity at the sampling locations

# DHANMONDI LAKE

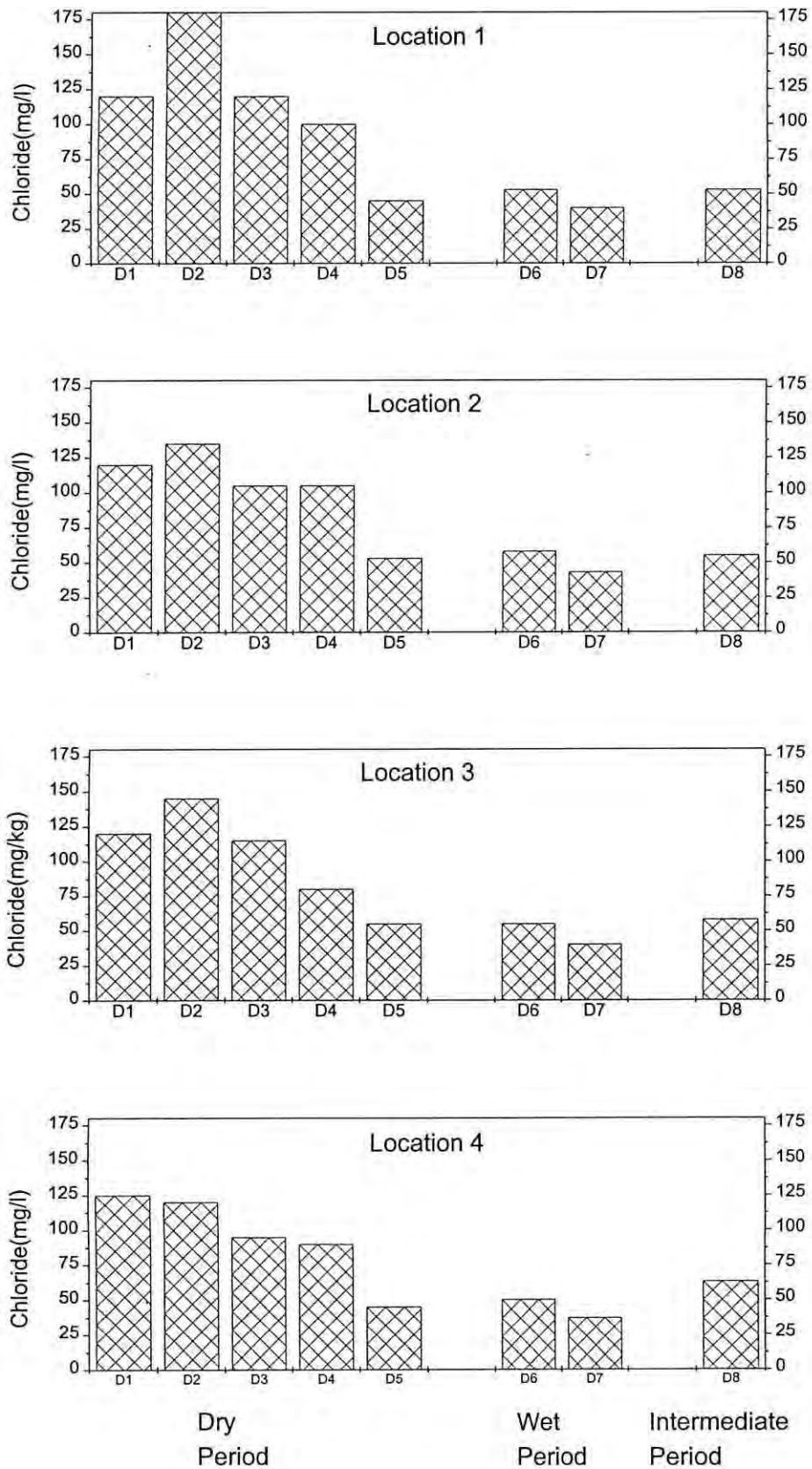


Fig.4.12 : Seasonal variation of chloride at the sampling locations



# DHANMONDI LAKE

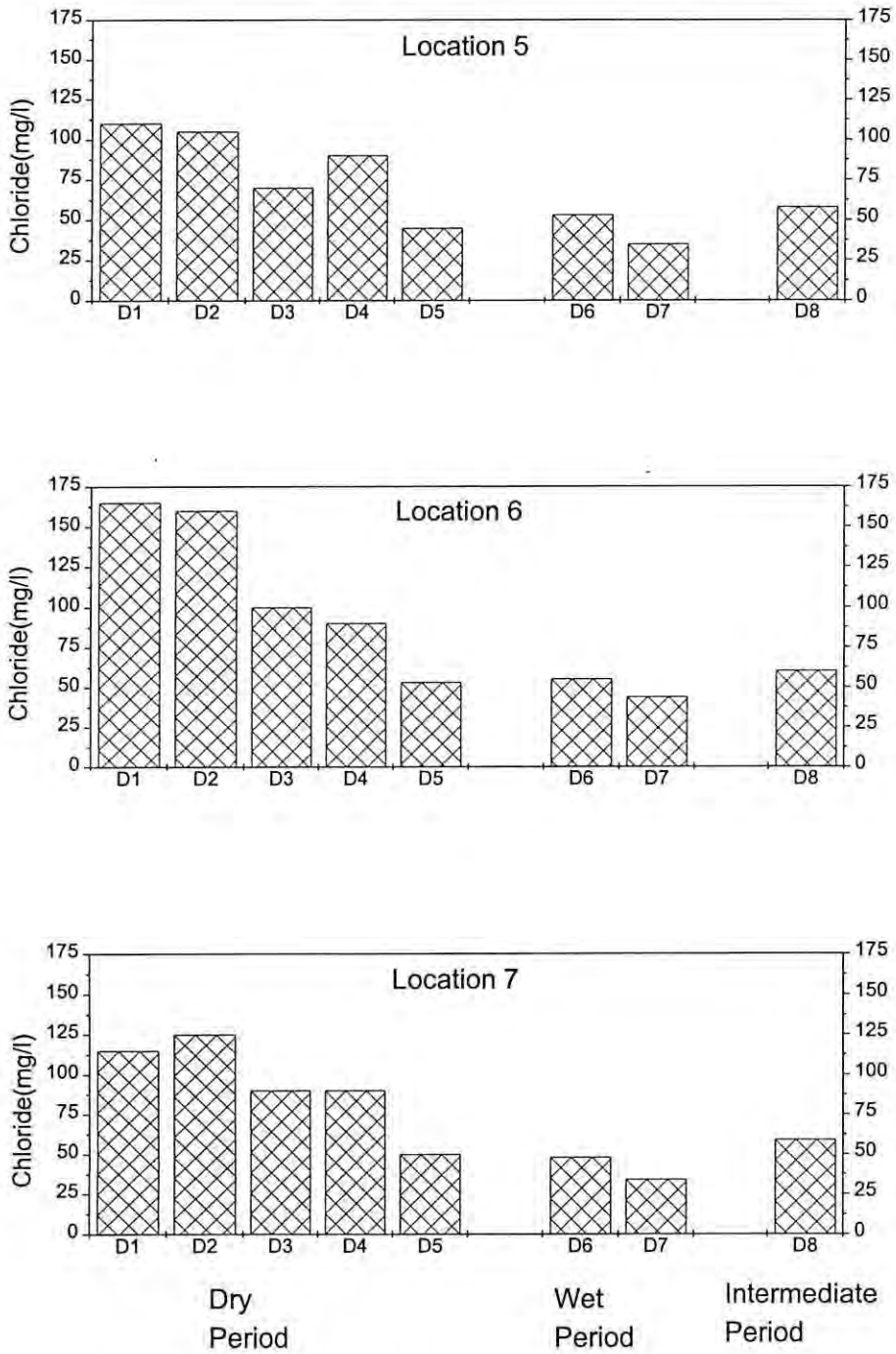


Fig.4.13 : Seasonal variation of chloride at different sampling locations

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# RAMNA LAKE

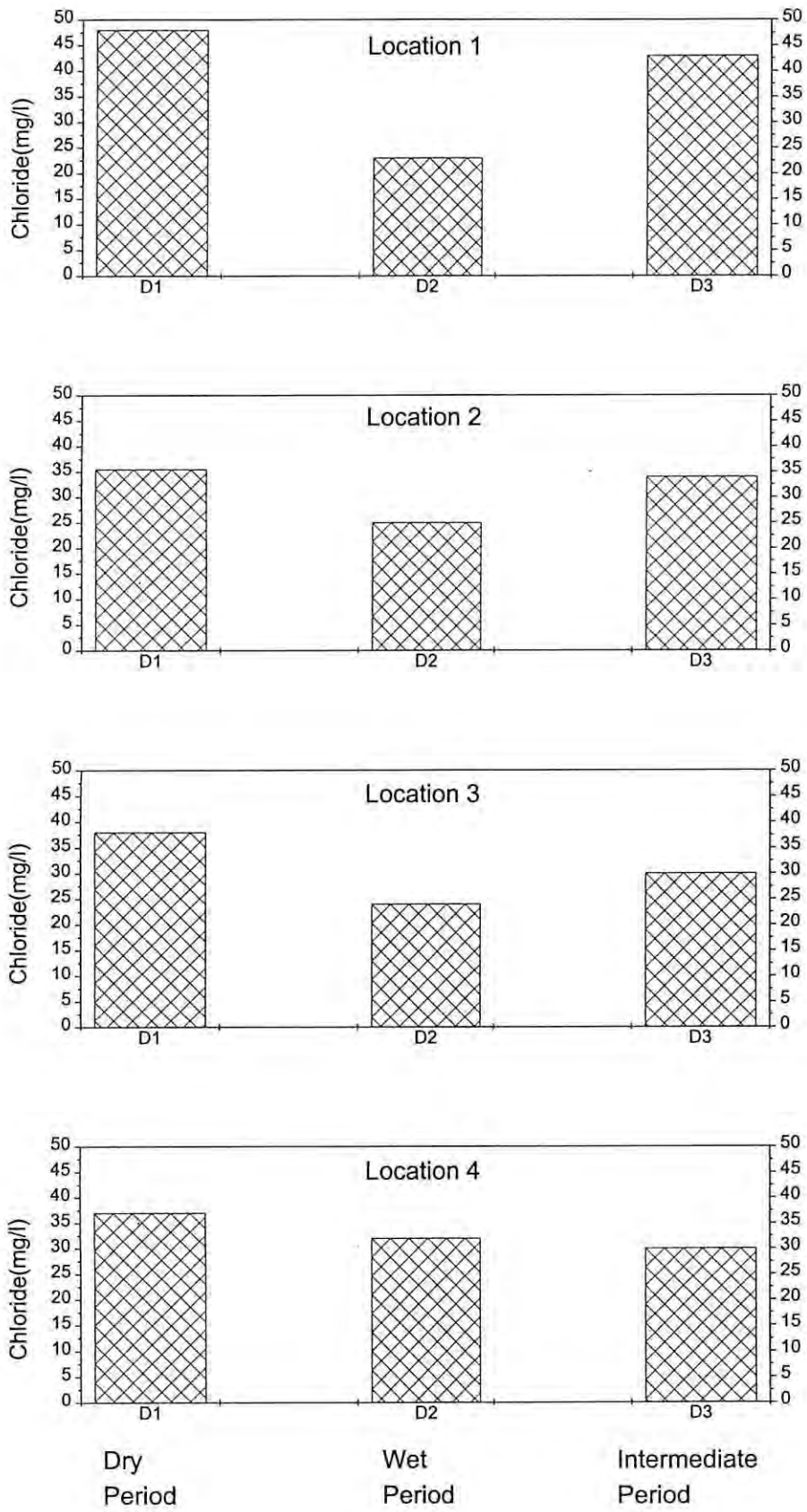


Fig.4.14 : Seasonal variation of chloride at sampling locations

#### 4.1.4 Variation of Nitrate and Phosphate

In this study, nitrate and phosphate tests were performed for limited number of samples as analysis could not be performed on all samples due to technical difficulties. Test results are given in Table 4.7. Nitrate concentration in Dhanmondi lake is around 2.03 mg/l while in Ramna lake it ranges from 0.5 to 8.2 mg/l. In case of phosphate the concentration ranges from 0.4 to 0.82 in Dhanmondi lake while 0.76 to 5.2 mg/l in Ramna lake.

#### 4.1.5 Variation of Sulfate

Tab. 4.8, Fig. 4.15 and Fig. 4.16 show seasonal variation of sulfate at different locations of Dhanmondi lake. Sulfate concentration during dry period varies from 13.4 to 118 mg/l, 12.5 to 145 mg/l in wet period, and 38.4 to 67.2 mg/l in intermediate period in Dhanmondi lake. Concentration of sulfate at different periods at sampling locations Ramna lake are shown in Fig. 4.17. This concentration ranged between 22.8 to 60.5 mg/l in dry period, 42.2 to 78.7 mg/l in wet period and 36.5 to 52.8 mg/l in intermediate period. In Dhanmondi lake, it was observed that at the end of dry period (day 5) and wet period, concentration of sulfate is relatively higher than other period. Concentration of sulfate is also high during wet period in Ramna lake. This probably indicates that atmospheric deposition from automobile exhaust and industrial emissions are the major source of sulfate in surface water. Increased rainfall at the end of dry period and in wet period brings in more sulfate into the lake that overcompensates the dilution effect. Since sulfate is known to form chemical complexes with copper, its presence is likely to influence speciation of copper in water.

Table 4.7: Variation of Phosphate & Nitrate at different periods at the sampling locations :

| DHANMONDI LAKE |         |                   |     |                    |                   |      |      |      |
|----------------|---------|-------------------|-----|--------------------|-------------------|------|------|------|
| Sampling       | Date    | P-1               | P-2 | P-3                | P-4               | P-5  | P-6  | P-7  |
| 1              | 4-4-96  |                   |     |                    |                   |      |      |      |
| 2              | 12-4-96 |                   |     |                    |                   |      |      |      |
| 3              | 15-5-96 |                   |     |                    |                   |      |      |      |
| 4              | 17-5-96 | 0.4               |     |                    |                   |      |      |      |
| 5              | 31-5-96 |                   |     |                    |                   |      |      |      |
| 6              | 4-6-96  |                   |     |                    |                   |      |      |      |
| 7              | 7-6-96  |                   |     |                    | 0.8               | .055 | 0.82 | 0.55 |
| 8              | 27-1-97 |                   |     |                    |                   |      |      |      |
| RAMNA LAKE     |         |                   |     |                    |                   |      |      |      |
| 1              | 24-5-96 |                   |     |                    | 1.6(P),<br>1.3(N) |      |      |      |
| 2              | 16-6-96 | 5.2(P),<br>8.2(N) |     |                    |                   |      |      |      |
| 3              | 27-1-97 |                   |     | 0.76(P),<br>0.5(N) |                   |      |      |      |

Table 4.8: Variation of sulfate (mg/l) at different periods at the sampling locations :

| DHANMONDI LAKE |         |       |      |      |       |      |      |      |
|----------------|---------|-------|------|------|-------|------|------|------|
| Sampling       | Date    | P-1   | P-2  | P-3  | P-4   | P-5  | P-6  | P-7  |
| 1              | 4-4-96  | 37.1  | 35.5 | 16.3 | 106.6 | 79.7 | 20.2 | 37.4 |
| 2              | 12-4-96 | 28.8  | 34.6 | 72   | 30.7  | 67.2 | 71   | 57.6 |
| 3              | 15-5-96 | 17.28 | 32.6 | 30.7 | 59.5  | 25   | 19.2 | 44.2 |
| 4              | 17-5-96 | 27.84 | 33.6 | 13.4 | 56.6  | 22   | 24   | 24   |
| 5              | 31-5-96 | 110   | 68   | 80   | 114   | 110  | 118  | 110  |
| 6              | 4-6-96  | 34.6  | 27.8 | 80.6 | 68.2  | 12.5 | 59   | 81.6 |
| 7              | 7-6-96  | 37.4  | 62.4 | 39.4 | 51.8  | 89.3 | 78.7 | 145  |
| 8              | 27-1-97 | 46.1  | 60.5 | 67.2 | 61.5  | 57.6 | 67.2 | 38.4 |
| RAMNA LAKE     |         |       |      |      |       |      |      |      |
| Sampling       | Date    | P-1   | P-2  | P-3  | P-4   |      |      |      |
| 1              | 24-5-96 | 22.8  | 44.1 | 60.5 | 52.8  |      |      |      |
| 2              | 16-6-96 | 49.9  | 42.2 | 78.7 | 52.8  |      |      |      |
| 3              | 27-1-97 | 36.5  | 45.1 | 42.2 | 52.8  |      |      |      |



# DHANMONDI LAKE

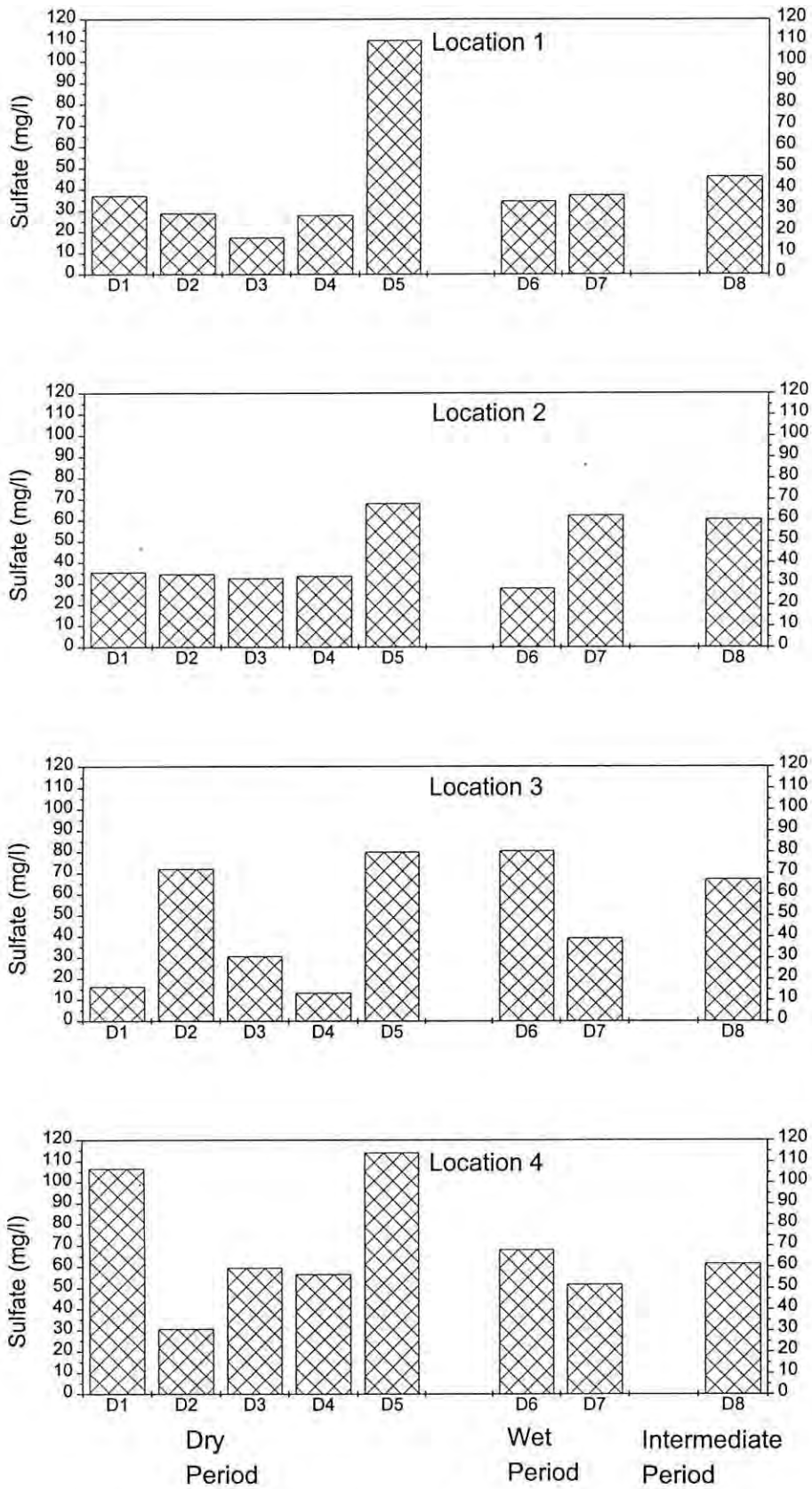


Fig.4.15 :Seasonal variation of sulfate at sampling locations

## DHANMONDI LAKE

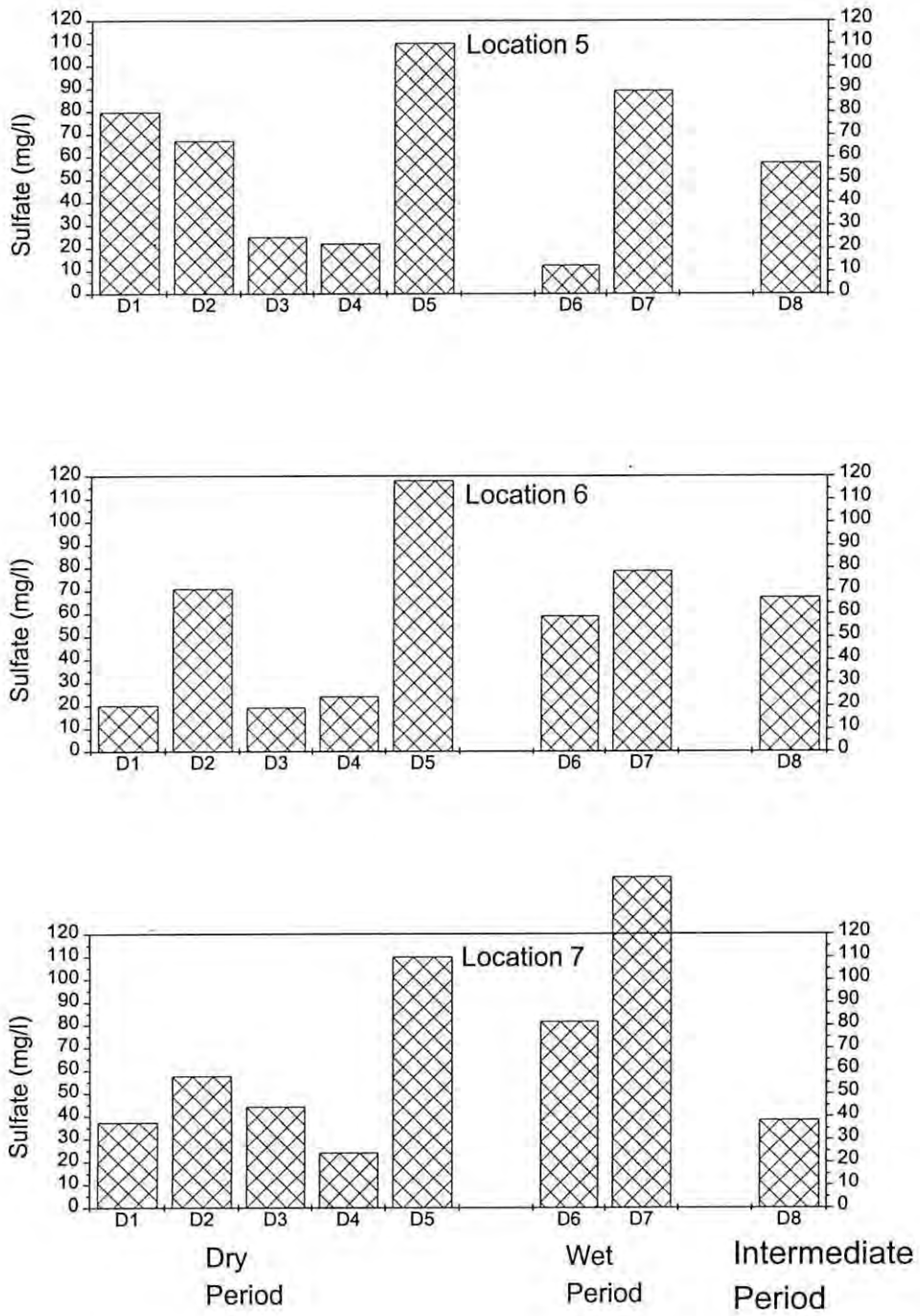


Fig.4.16: Seasonal variation of sulfate at sampling locations

# RAMNA LAKE

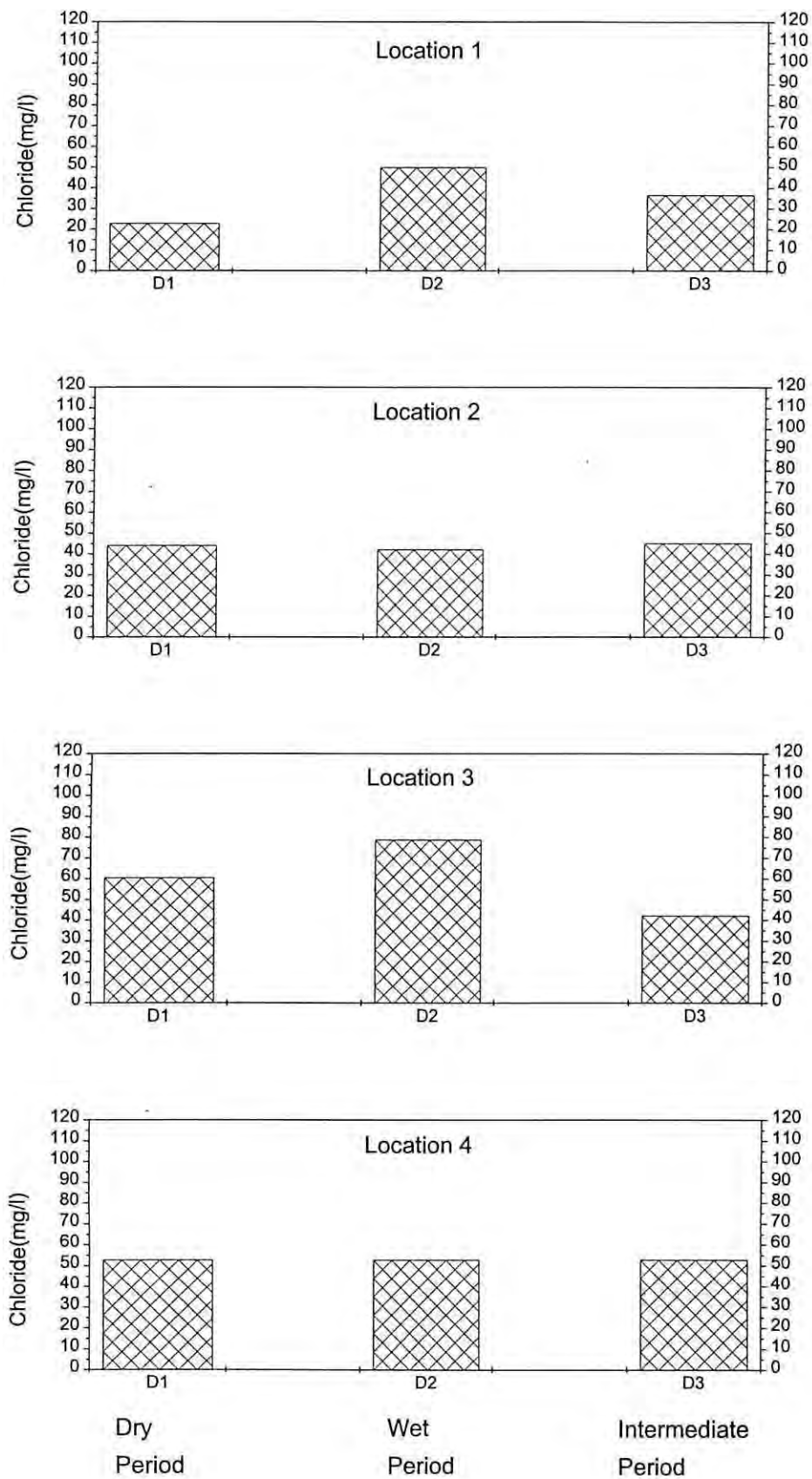


Fig. 4.17: Seasonal variation of sulfate at sampling locations

## 4.2 EQUILIBRIUM SPECIATION

### 4.2.1 Chemical Speciation and Equilibrium Model

For a particular water body, “perfect” understanding of the chemical behavior of natural waters would require a knowledge of the concentration of all chemical species at all time and in all places. However, it is often justified, for all practical purposes, to assume that the reactions occurring in the system have reached equilibrium. Chemical Equilibrium often provides a good approximation of the compositions of natural waters. It also provides information on the direction of spontaneous changes.

Many chemical reactions taking place in natural water are quite fast and can be considered to be at equilibrium. For example, the acid base reactions of carbonate species are complete within seconds or minutes, well within the time frame for most of our observations. By ignoring slow reactions, such as gas exchanger mineral dissolution, one obtains a partial equilibrium model of the real system, which includes some kinetic reactions just by the choice of the reactions considered to take place. On the other hand, a kinetic description of chemical reactions that are neither very fast nor very slow, can under certain conditions, be superimposed on an equilibrium model for fast reactions. This is called a pseudo equilibrium model. In this way one can describe the variations in the carbonate chemistry and pH of a lake by calculating the atmospheric exchange of  $\text{CO}_2$  with time and maintaining equilibrium among the dissolved species.

The fate of trace pollutants (such as heavy metals) in natural water is often controlled by adsorption reaction with mobile and fixed adsorbents. Potential adsorbents in aquatic systems comprise biotic (e.g. algae, bacterial, zooplankton) and abiotic particles, both organic and inorganic. The most common inorganic adsorbents are hydrous metal oxides, clays and carbonates, while the most common organic adsorbents consists of plant and animal remains and humic coating on mineral surfaces (Dzombak and Morel, 1987). Among the inorganic adsorbents, hydrous metal oxides have the highest affinity for ions because of their charge, reactive hydroxyl surface sites combined with their high surface area. Hydrous oxides are also prevalent as coating on all types of particles, including



clays (whose edges have an oxide structure), other mineral phases, particular organic matter, and even the surface of algal cells.

Absorption on trace inorganic solutes (e.g. heavy metals), mostly irons, is conceived as a chemical coordinating process involving specific interaction between solutes and reactive surface groups. Thus inorganic adsorption models must represent these specific interactions explicitly and also describe the interrelation between electrostatic charge development on solid surfaces and in adsorption. In recent years, surface complexation models (SCM), have been widely successful for describing adsorption of inorganic solutes on oxide surfaces. In this (SCM) approach, adsorbing ions are considered to react chemically with specific surface hydroxyl groups, after coming through the interfacial electric field at the surface. The electric field which may be positive or negative, results from a positive or negative surface charge caused by the chemical reactions at the surface. Although a number of variations of the basic surface complexation approach have been developed, the fundamental concepts upon which all complexation models are based remain the same (Dzombak and Morel, 1987):

- Sorption on oxides takes place at specific coordination sites.
- Sorption reactions on oxides can be described quantitatively via mass law equation.
- Surface charge on oxides results from sorption reaction themselves.
- The effect of surface charge on sorption can be taken into account by applying a correction factor derived from the Electric Double Layer (EDL) theory to mass law constants for surface reactions.

The most widely used surface complexation models are the Constant Capacitance Model, the generalized Two layer Model and the Triple layer Model.

Once a system is defined with all its possible variations (i.e. all its chemical reactions including adsorption reactions), its equilibrium state is uniquely defined. The equilibrium composition of the system can be determined by solving the mass law and mass balance

equation simultaneously. A number of chemical equilibrium models (e.g. MINEQL+, Schecher, 1994) are available for solving chemical equilibrium.

#### **4.2.2 Equilibrium Speciation of Copper in Dhanmondi and Ramna Lakes**

Dhanmondi and Ramna lake, situated in the central Dhaka, receive contaminant from a wide range of sources, such as domestic and industrial waste water, pollutants with rainfall in the form of surface run-off. In most studies dealing with heavy metal pollution, only soluble (dissolved) and particulate concentration are reported. Very little consideration is given to the distribution of trace metals among various aqueous species solid phases. This distribution referred to as speciation is particularly important for trace metals, because knowledge of chemical forms of a trace metal is essential for estimating its biological activity, physico chemical reactivity and toxicity. Heavy metals, such as Cu, are usually present in natural water in various forms, e.g. as free ion, as complex with organic and inorganic ligands or in sorbed state on aquatic particles, such as hydrous metal oxides and particulate organic matter. All the chemical forms of a specific heavy metal are not toxic when threshold concentration are exceeded. For example, for any toxic metals, the thumb rule is that the free form is more toxic than the complexed forms.

Chemical composition of lake-water was determined (see Art. 4.1.1 to 4.2.1) at seven sampling locations in Dhanmondi lake and four sampling locations in Ramna lake. Using the chemical composition data determined earlier, equilibrium speciation of Cu was determined using chemical equilibrium model MINEQL<sup>+</sup>. For each sampling locations speciation calculation were carried out for dry, wet and intermediate period. Speciation was performed without considering contribution from sediment and considering contribution from sediment. Seasonal variation in speciation has been assessed, major Cu species have been determined and their implication on copper pollution have been discussed.

In order to find out the species of Cu by using MINEQL<sup>+</sup> all the components (anionic and cationic) that could significantly influence the equilibrium of Cu were selected. The



components selected were  $\text{H}_2\text{O}$ ,  $\text{H}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{Cl}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  and  $\text{K}^+$ . Total concentration of these components were determined for seven sampling locations of Dhanmondi lake and four sampling locations of Ramna lake (along with their seasonal variation through laboratory analysis, results presented in Appendix B). It should be noted that concentration of DOC (dissolved organic carbon) or TOC (total organic carbon) and could not be determined in this study because of malfunctioning of the TOC analyzer. Concentration of other heavy metals were not determined, because preliminary laboratory test results suggested that other heavy metals are present in Dhanmondi lake in trace amount and are not likely to significantly influence speciation of copper in lake water.

Adsorption of copper on suspended and bottom sediments was defined by “Two Layer Adsorption” model using hydrous ferric oxide as sorbent. In the absence of data on particulate organic adsorbents, it can be reasonably assumed that hydrous metal oxides are primary sorbents for copper in lake water. To describe sorption copper and other ions on hydrous oxides, the generalized Two Layer Adsorption model (Dzombak and Morel, 1987) was used. However detailed characterization of oxide adsorbents is beyond the scope of this study. In fact, such characterization is extremely difficult. In this study, for describing partitioning (adsorption) of ionic solutes, a simplified approach was taken. Here adsorption was defined with the generalized two-layer model using hydrous ferric oxide (HFO) as adsorbent. HFO has very strong affinity for heavy metals such as copper. It is a major adsorbent in many aquatic environment (Dzombak and Morel, 1987). Adsorption reaction of a wide range of ionic sorbates including copper have been characterized and then reactions and their corresponding equilibrium constants have been included in the database of MINEQL+. Concentration of adsorbent (HFO) was varied in all cases until simulated concentration of aqueous (or adsorbed) copper matched the experimentally determined value. The advantage of using this model is that all adsorption reactions for HFO have already been characterized by Dzombak and Morel (1990) and are stored in the thermodynamic database of the model. In the absence of detailed information on adsorbent characteristics, this is a reasonable approximation.



The lake water was assumed to be in equilibrium with the atmospheric CO<sub>2</sub>. Although gas exchange reactions are usually slow, for all practical purposes this is a reasonable assumption. MINEQL+ has the option for simulating gas-exchange, and variation of ionic strength, temperature and pH. All the equilibrium analyses were performed for 25°C temperature, which is the expected temperature at the mid depth of lake water.

The basic assumptions used in the chemical equilibrium calculations, in this study, are:

1. Dissolved and particulate organic matter have negligible influence on speciation of copper,
2. Adsorption of copper can be described by the generalized two layer model using HFO as adsorbent,
3. Lake water is in equilibrium with atmospheric CO<sub>2</sub>,
4. Heavy metals other than copper has little influence on copper speciation.

As mentioned in Chapter 3, lake water samples for laboratory analysis were collected from mid depth, at the sampling locations. At the surface of the lake, adsorption/desorption to and from suspended solids would control partitioning of copper. Whereas, close to the bottom sediment, adsorption/desorption to or from the bottom sediment are also important.

To simulate copper speciation, two models were considered. In the first model, it was assumed that aqueous copper is in equilibrium with only the copper in suspended sediment. This would be the case for the portion of water column close to the surface of the lake. Copper present in the bottom sediment is ignored in this calculations. In the second model, it was assumed that the entire water column is in equilibrium. Bottom sediment as well as suspended sediment were considered to be involved in adsorption/desorption. It should be noted that for fixed pH calculation these two models would give similar results for speciation of aqueous species. However, if one wants to calculate change in speciation due to any change(e.g., addition of acid or alkali or copper containing waters), the results should reach equilibrium, the second model, with consideration of equilibrium for the entire system would give more realistic results.



## 4.3 RESULTS AND ANALYSIS

### 4.3.1 Speciation of Copper Without Considering Contribution From Sediment

Equilibrium analysis without considering any contribution of sediments for all seven sampling locations of Dhanmondi lake and four locations of Ramna lake during dry, wet and intermediate period, were performed by MINEQL+. Computational outputs are listed in Appendix B and C. Concentration of various species, given in the output, are expressed in moles/liter.

#### *Copper Speciation in Dhanmondi Lake*

Fig 4.18 through 4.24 show bar charts concentrations and relative proportions in pie charts of the major species of Cu present in aqueous media of Dhanmondi lake for all seven sampling locations during dry and, wet and intermediate period. In these figures, bar charts have been used to represent total concentration (in moles/liter) of each species and also concentration of Cu adsorbed on suspended sediment. Pie charts represent the proportion of various copper species and Cu adsorbed on suspended sediment with respect to total Cu species. The major Cu species that dominates in all cases is aqueous  $\text{Cu}(\text{OH})_2$ . The amount of copper adsorbed on suspended sediment is also high. Other species that are present in small quantities are  $\text{Cu}^{2+}$ , aqueous  $\text{CuCO}_3$ ,  $\text{CuOH}^+$ .

Fig. 4.18 shows the concentration and proportion of copper species present at location 1. Concentration and proportion of major Cu species aqueous  $\text{Cu}(\text{OH})_2$  as well as Cu adsorbed on suspended sediment are higher during dry period than wet or intermediate period.  $\text{Cu}^{2+}$  and aqueous  $\text{CuCO}_3$  are also present in significant amount. From pie chart, it is evident that proportion of aqueous  $\text{Cu}^{2+}$  is higher during dry period than wet period. This may result due to the difference of pH between two seasons (pH 7.66 in dry period and 7.8 in wet period). But for the case of aqueous  $\text{CuCO}_3$  it is found that proportion of aqueous  $\text{CuCO}_3$  in dry period is lower than wet or intermediate period (pH 7.8). Probably an increase in pH promote complexation of copper with carbonate species.

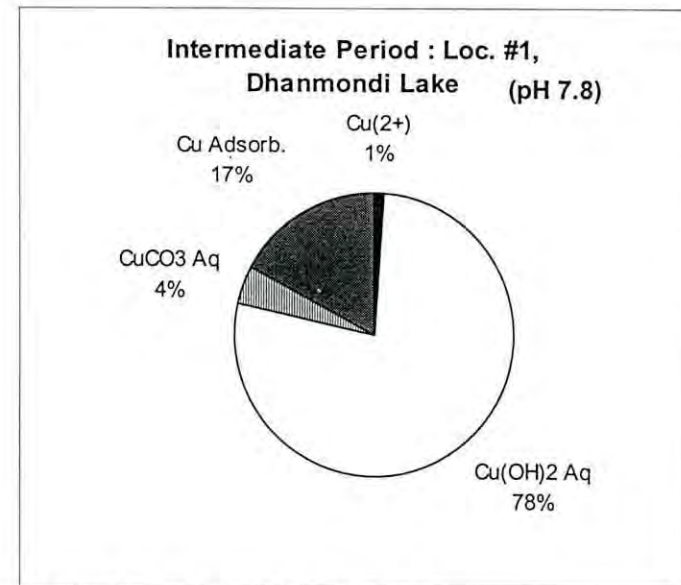
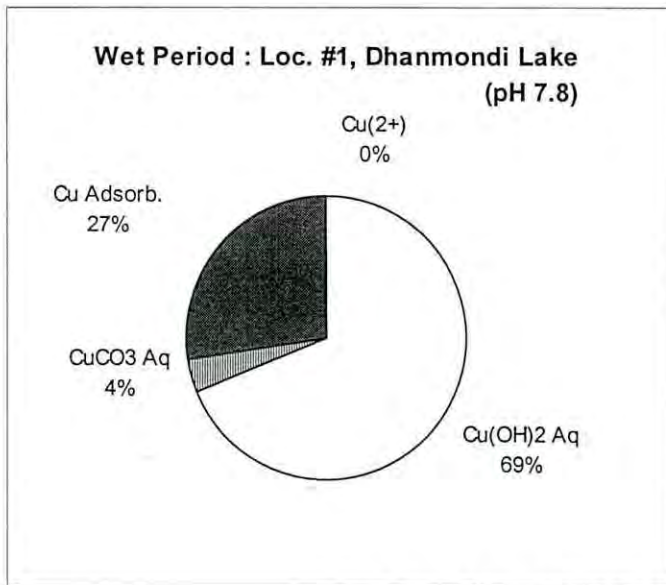
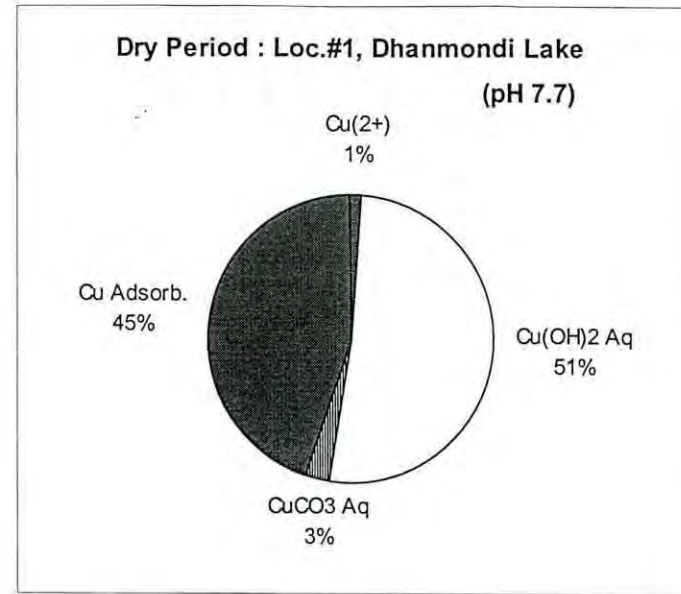
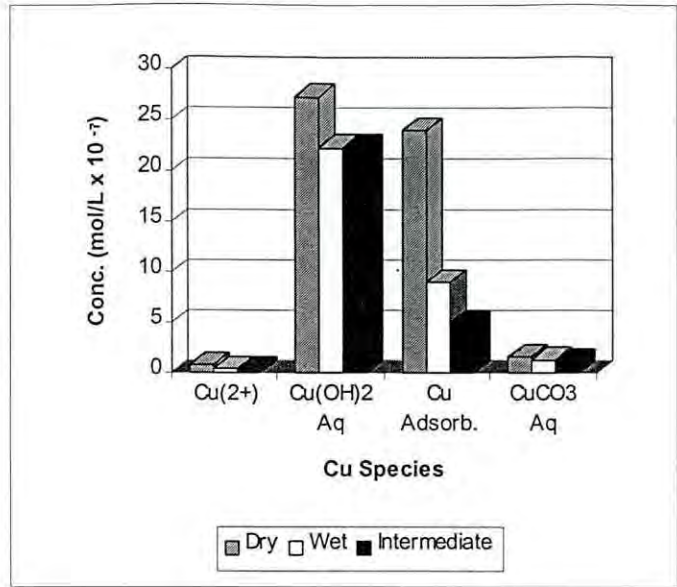


Figure 4.18:- Major Cu species without contribution from sediment (Location 1)

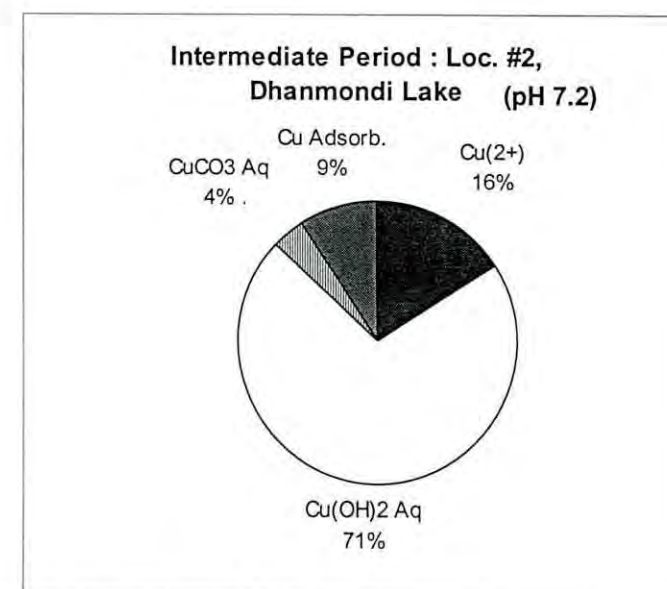
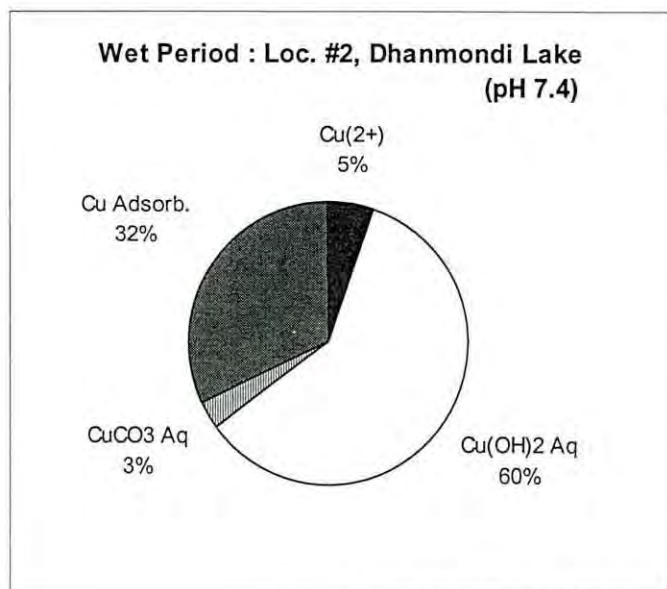
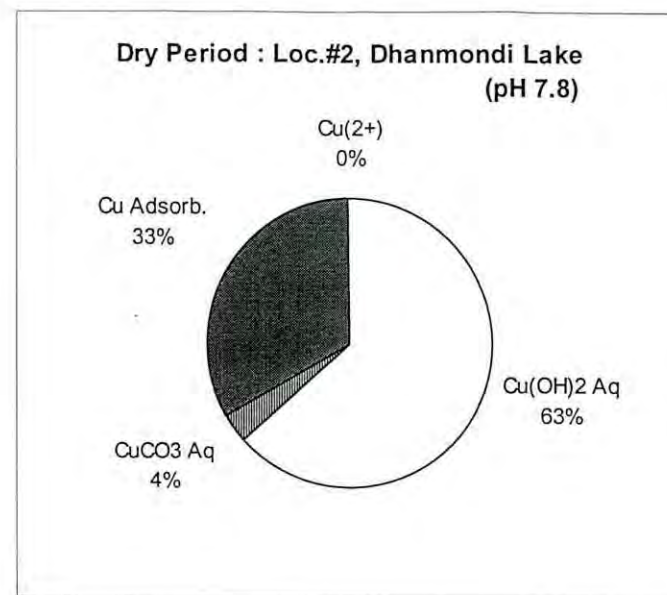
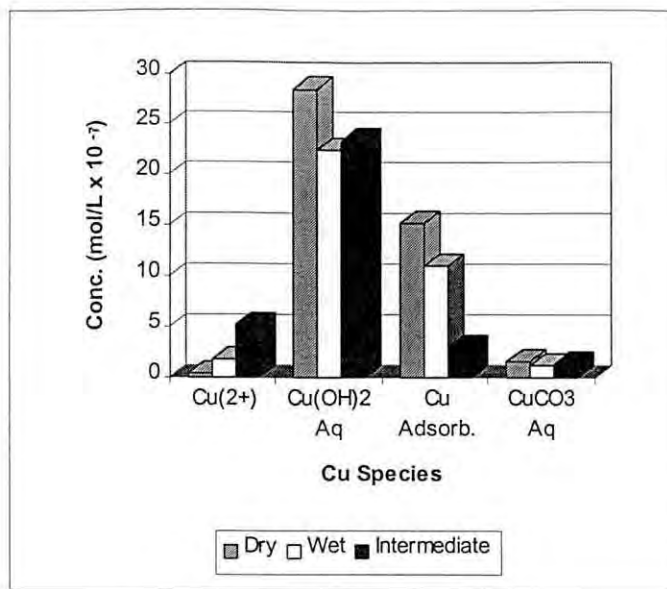


Figure 4.19 : Major Cu species without contribution from sediment (Location 2)

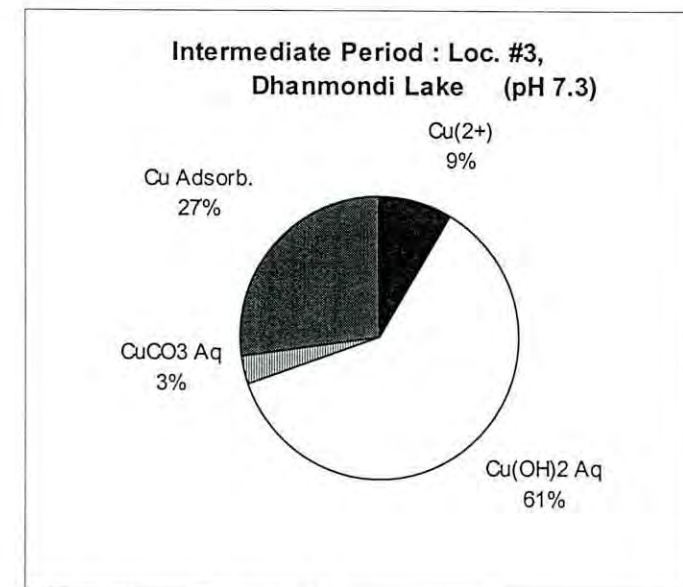
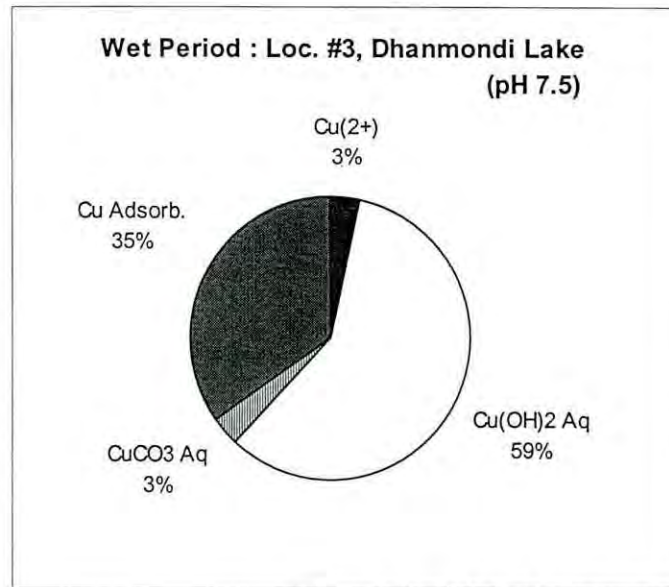
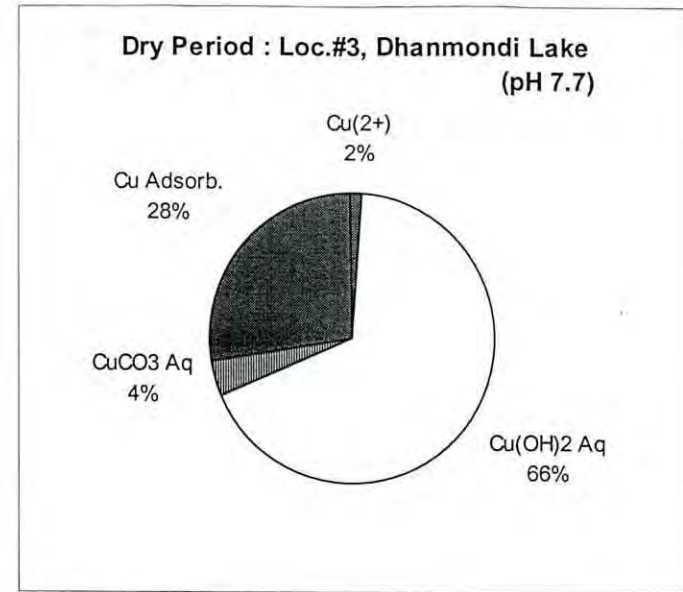
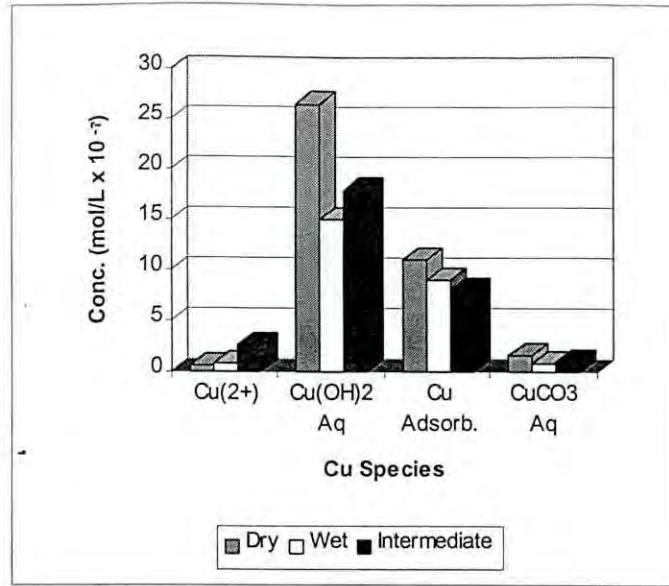


Figure 4.20 :- Major Cu species without contribution from sediment (Location 3)



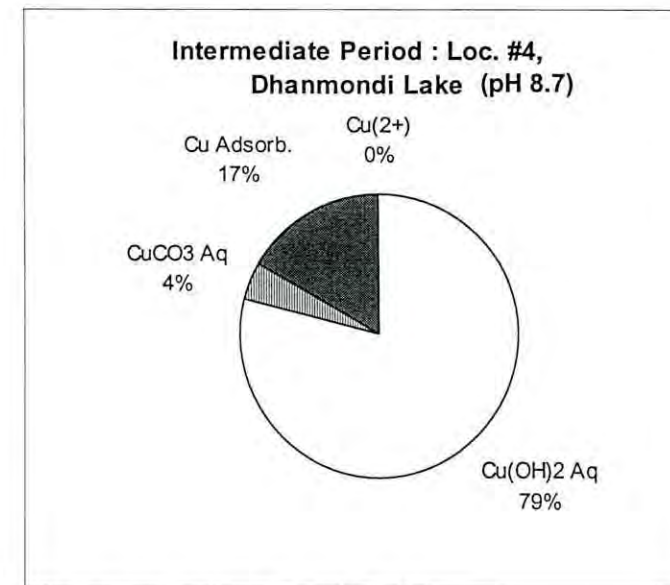
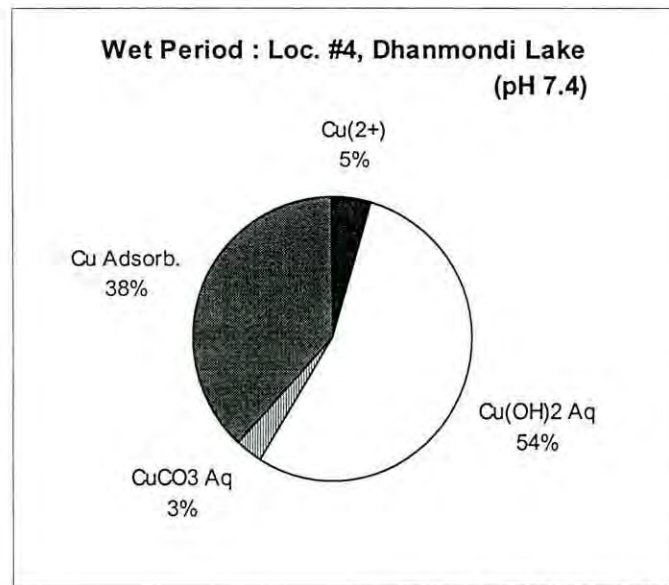
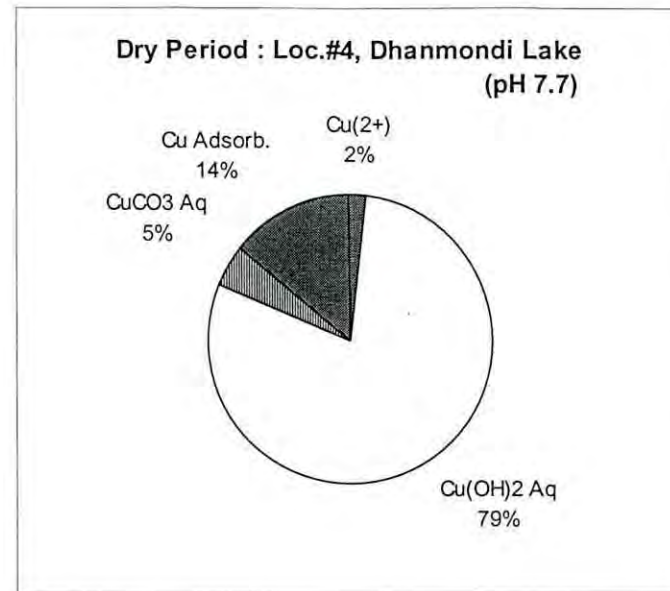
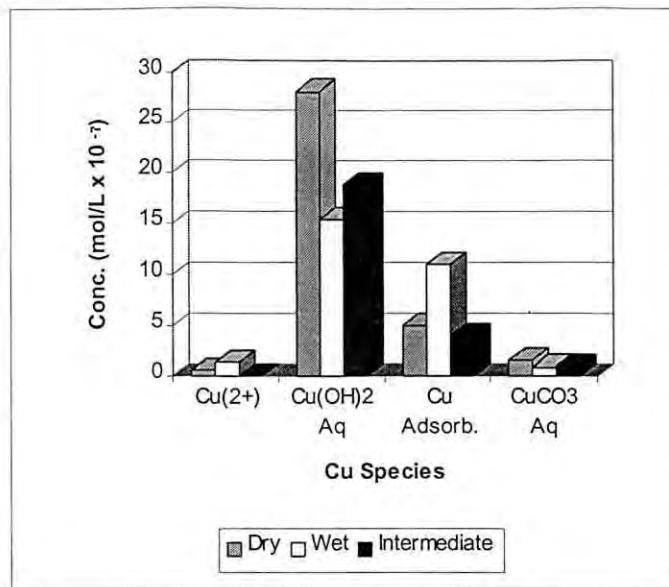


Figure 4.21 : Major Cu species without contribution from sediment (Location 4)

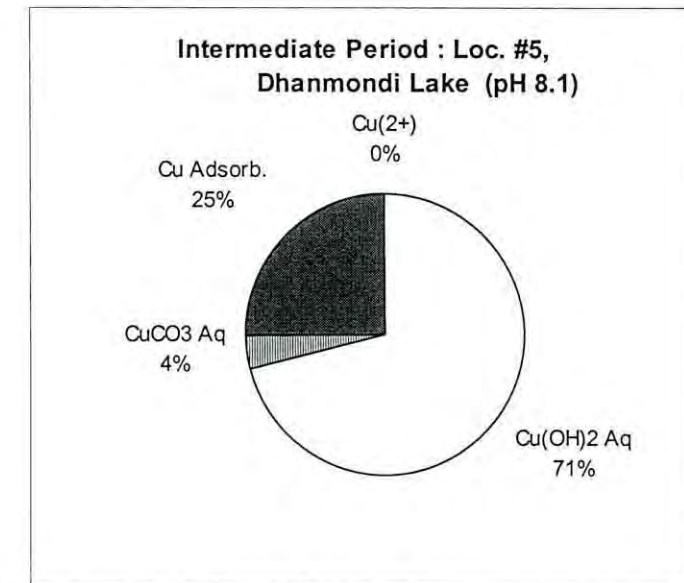
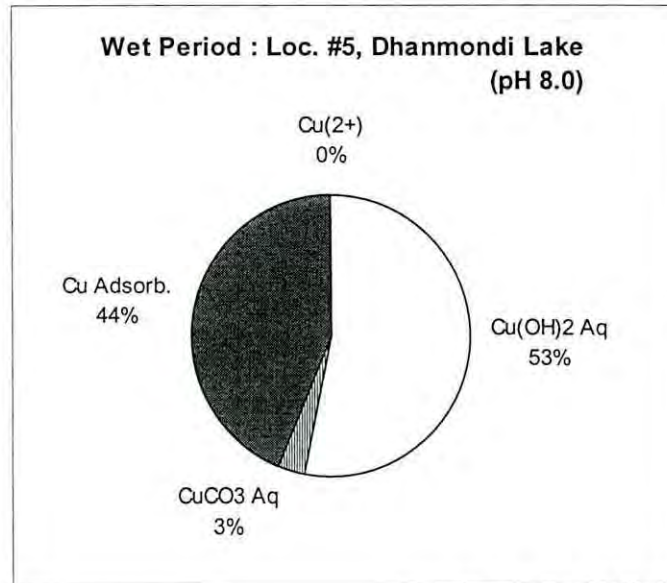
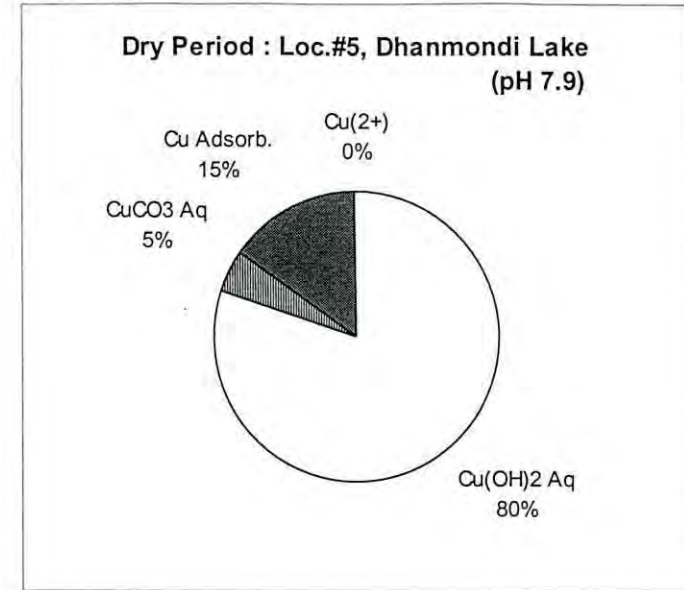
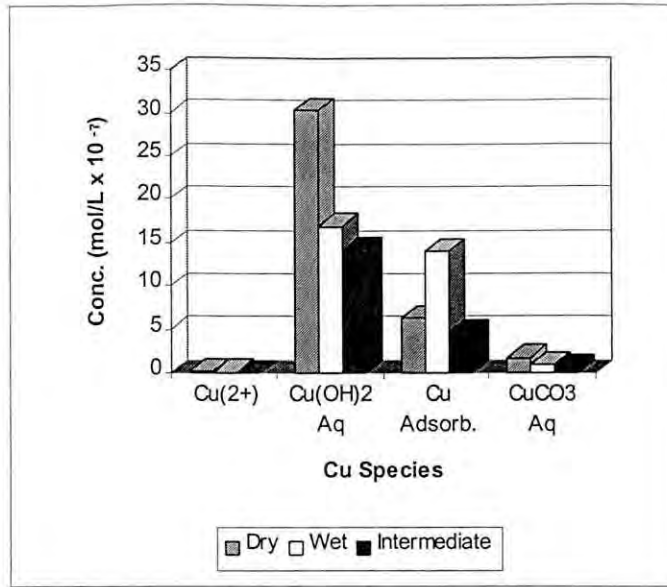


Figure 4.22 : Major Cu species without contribution from sediment (Location 5)

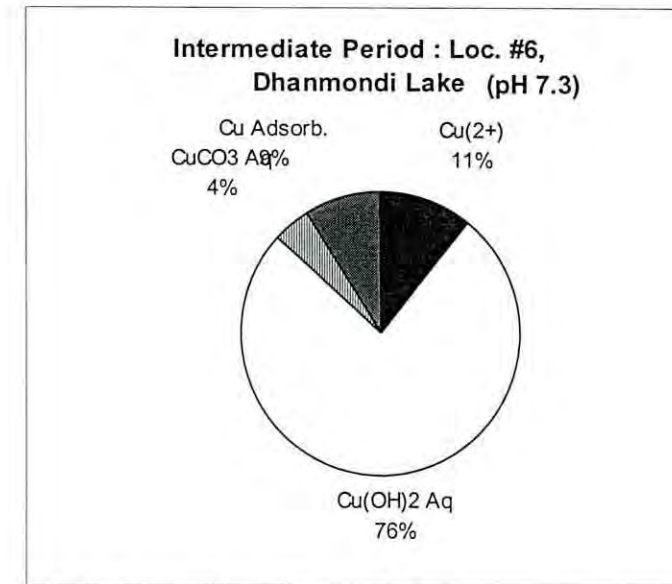
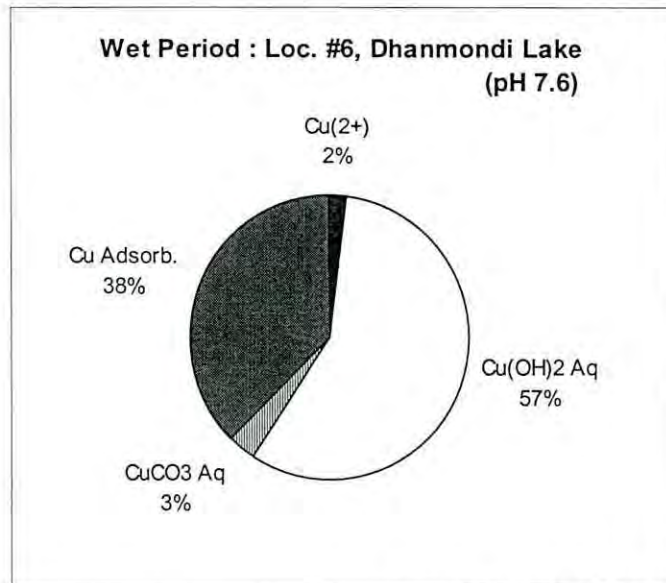
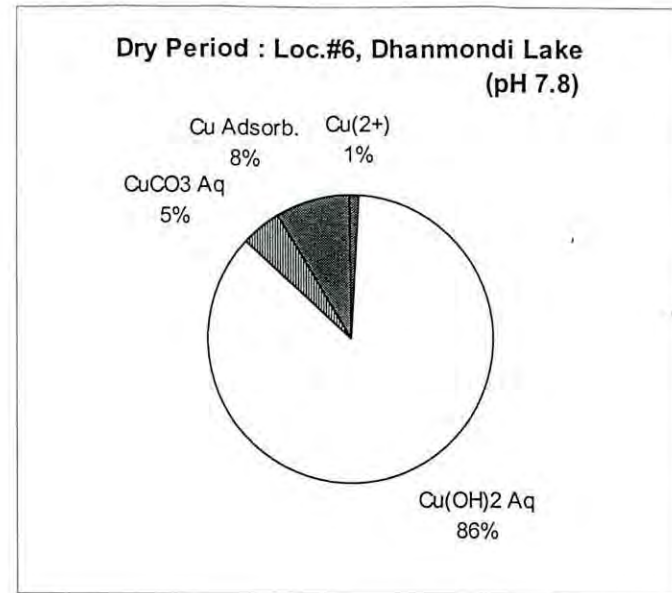
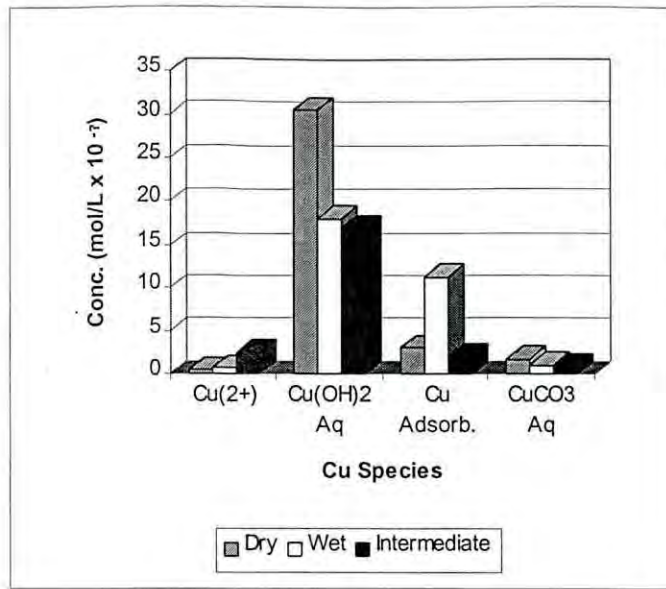


Figure 4.23 : Major Cu species without contribution from sediment (Location 6)

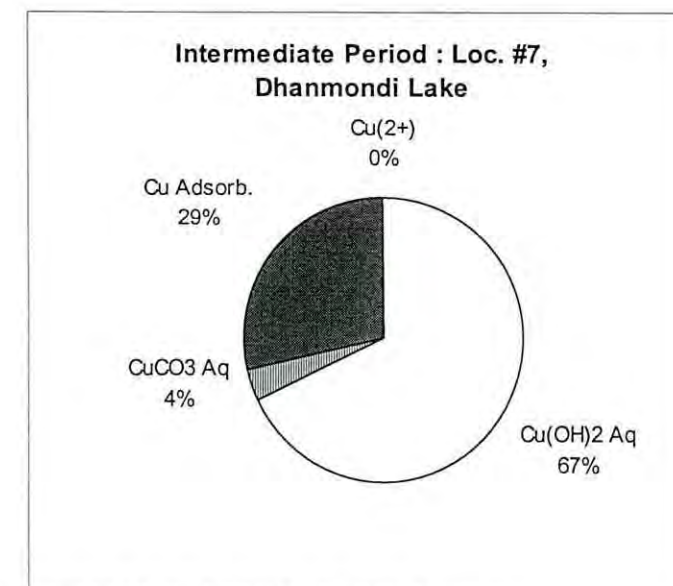
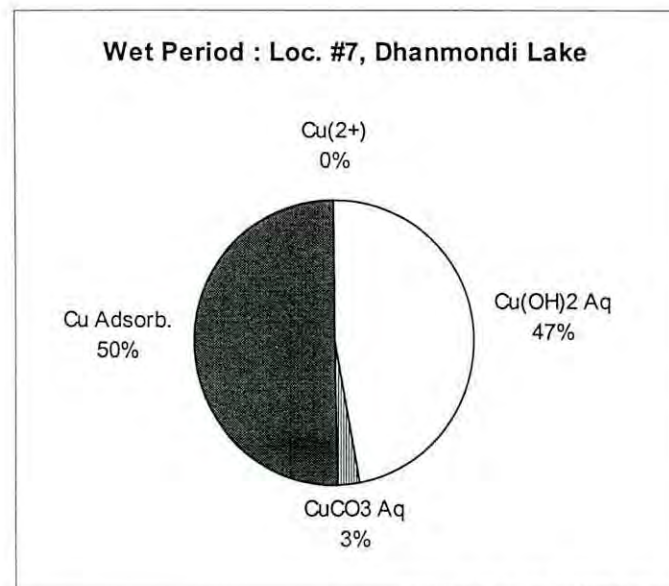
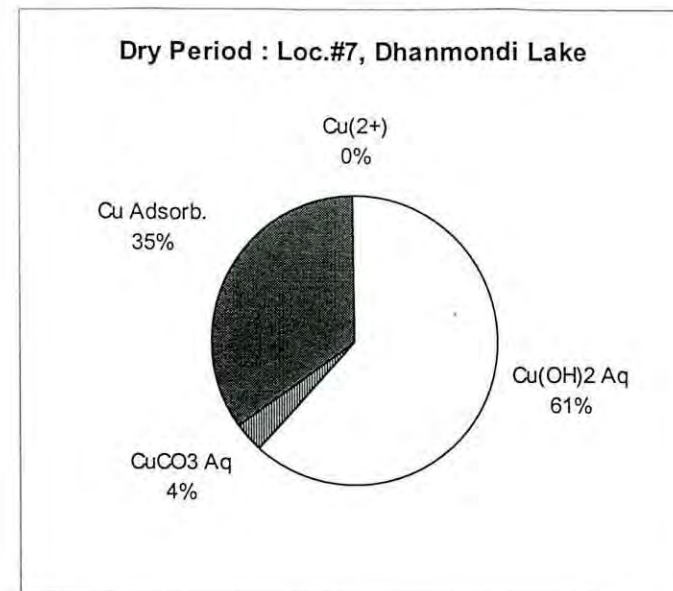
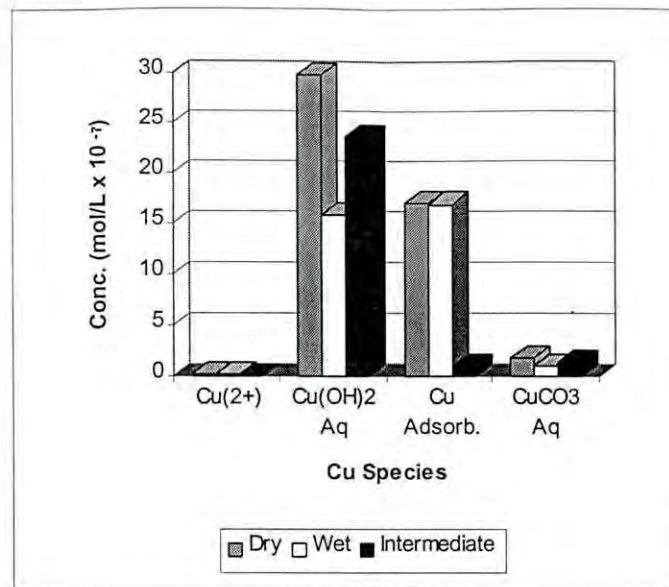


Figure 4.24 : Major Cu species without contribution from sediment (Location 7)



Concentration of aqueous  $\text{Cu}(\text{OH})_2$  ranges from  $2.23\text{e}^{-6}$  to  $2.73\text{e}^{-6}$  mol/l (i.e. 218  $\mu\text{g/l}$  to 266  $\mu\text{g/l}$ ) and  $\text{Cu}^{2+}$  from  $3.12\text{e}^{-8}$  to  $7.42\text{e}^{-8}$  mol/l (i.e. 1.98  $\mu\text{g/l}$  to 4.72  $\mu\text{g/l}$ ) during the three periods.

Fig. 4.19 shows concentration and relative proportion of Cu species at Location 2. Aqueous  $\text{Cu}(\text{OH})_2$  shows similar trend as the major species. Concentrations of aqueous  $\text{Cu}(\text{OH})_2$  and adsorbed Cu in dry period is higher than those during other periods. From the pie chart, proportion of  $\text{Cu}^{2+}$  in dry period is less than wet period and proportion of  $\text{Cu}^{2+}$  in wet period is less than intermediate period. This may be due to the difference of pH values (pH in dry period is 7.8, in wet period 7.4 and in intermediate period 7.2). Proportion of aqueous  $\text{CuCO}_3$  is higher in dry period than wet period which may also be attributed due to relatively higher pH in dry period. Concentration of aqueous  $\text{Cu}(\text{OH})_2$  varies from  $2.04\text{e}^{-6}$  to  $2.85\text{e}^{-6}$  mol/l (i.e. 199  $\mu\text{g/l}$  to 278  $\mu\text{g/l}$ ) and  $\text{Cu}^{2+}$  from  $4.08\text{e}^{-7}$  to  $5.26\text{e}^{-7}$  (i.e. 26  $\mu\text{g/l}$  to 33  $\mu\text{g/l}$ ).

Fig. 4.20 to Fig 4.24 concentrations and relative proportions of Cu species and Cu adsorbed on suspended sediment at location 3, 4, 5, 6 and 7. In all the cases aqueous  $\text{Cu}(\text{OH})_2$  was the major species.  $\text{Cu}(\text{OH})_2$  was always higher during dry period than those during other periods. Except for location 3, concentration of adsorbed Cu during wet period is higher than that of other periods at other locations.  $\text{Cu}^{2+}$  and aqueous  $\text{CuCO}_3$  show similar trend following the pH trend. For all these locations concentration of aqueous  $\text{Cu}(\text{OH})_2$  varies from  $1.41\text{e}^{-6}$  to  $3.05\text{e}^{-6}$  mol/l (i.e. 138  $\mu\text{g/l}$  to 98  $\mu\text{g/l}$ ) and  $\text{Cu}^{2+}$  varies from  $4.16\text{e}^{-10}$  to  $25.2\text{e}^{-8}$  mol/l (i.e. 0.03  $\mu\text{g/l}$  to 16  $\mu\text{g/l}$ ).

From the results of Cu speciation shown in Fig. 4.18 through Fig. 4.24, it is quite clear that pH has great influence on speciation of aqueous Cu. For example at Location 3 during dry period where pH is 7.7, percentage of  $\text{Cu}^{2+}$ , aqueous  $\text{Cu}(\text{OH})_2$  and aqueous  $\text{CuCO}_3$  are 2%, 66%, and 4%. At location 2, at pH 7.8, during dry period these percentage are 1%, 63% and 4%. At location 7, during wet period (pH 7.9) these percentage become 0%, 61% and 4%. So it is evident that the proportions of various species of Cu in Dhanmondi lake depend too large extent on pH of water.  $\text{Cu}^{2+}$  and

aqueous  $\text{Cu}(\text{OH})_2$  decreases with the increase of pH value. Aqueous  $\text{CuCO}_3$  increases with the increase of pH.

### ***Copper Speciation in Ramna Lake***

Fig. 4.25 to Fig. 4.28 show the concentrations (bar chart) and relative proportions (pie chart) of species of Cu in aqueous media and Cu adsorbed on suspended sediment during dry, wet and intermediate period. Bar charts represent total concentrations (in moles/l) of each species and pie charts represent relative proportion of each species. Aqueous  $\text{Cu}(\text{OH})_2$  is found to be the major species in all cases. Other species of Cu found include  $\text{Cu}^{2+}$ , adsorbed Cu, and aqueous  $\text{CuCO}_3$ .

Fig. 4.25 shows concentration and relative proportion of species of Cu at Location 1 of the Ramna lake. Concentration of aqueous  $\text{Cu}(\text{OH})_2$  during dry period was higher than those in wet and intermediate period. Concentration of aqueous  $\text{CuCO}_3$  during dry period was higher than those during other periods. However,  $\text{Cu}^{2+}$  and adsorbed Cu concentration of these species was higher during intermediate period than other periods. From the pie charts, proportion of  $\text{Cu}^{2+}$  was higher during wet period (pH 7.3) than dry period (pH 8.7) and  $\text{Cu}^{2+}$  during intermediate (pH 7.1) is higher than wet period. Thus, proportion of  $\text{Cu}^{2+}$  increases with decrease of pH is also evident. Relative proportion of aqueous  $\text{CuCO}_3$  was higher during dry period (pH 8.7) than the wet period (pH 7.3) and proportion of aqueous  $\text{CuCO}_3$  is lowest during intermediate period (pH 7.1). A trend similar to that of the Dhanmondi lake was observed  $\text{Cu}^{2+}$  and aqueous  $\text{CuCO}_3$  where the first one increases with the decrease of pH and the later one increases with increase of pH. Concentration of aqueous  $\text{Cu}(\text{OH})_2$  varies from  $2.72 \times 10^{-6}$  to  $0.85 \times 10^{-6}$  mol/l (i.e. 265  $\mu\text{g/l}$  to 83  $\mu\text{g/l}$ ) and  $\text{Cu}^{2+}$  from  $0.46 \times 10^{-6}$  to  $5.87 \times 10^{-10}$  mol/l (i.e 29  $\mu\text{g/l}$  to 0.04  $\mu\text{g/l}$ ).

Fig. 4.26 shows concentrations of Cu species and their relative proportion at Location 2 of the Ramna lake. Concentration of the major Cu species aqueous  $\text{Cu}(\text{OH})_2$  is higher than those of the other periods. Concentration of  $\text{Cu}^{2+}$  was highest during intermediate period and  $\text{CuCO}_3$  aq is highest in dry period. From the pie chart, relative proportion of  $\text{Cu}^{2+}$  was found to be lowest in dry period (pH 8.9) than wet period (pH 7.4) and intermediate period (pH 7.5). A deviation in proportion of  $\text{Cu}^{2+}$  was observed. Though

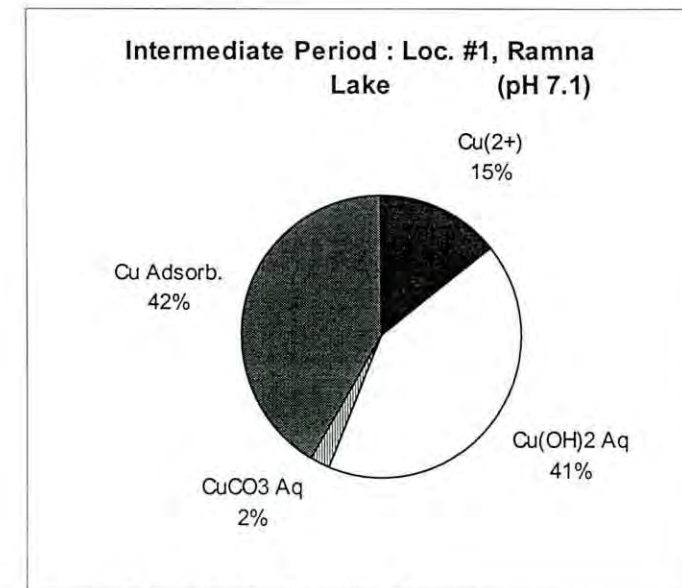
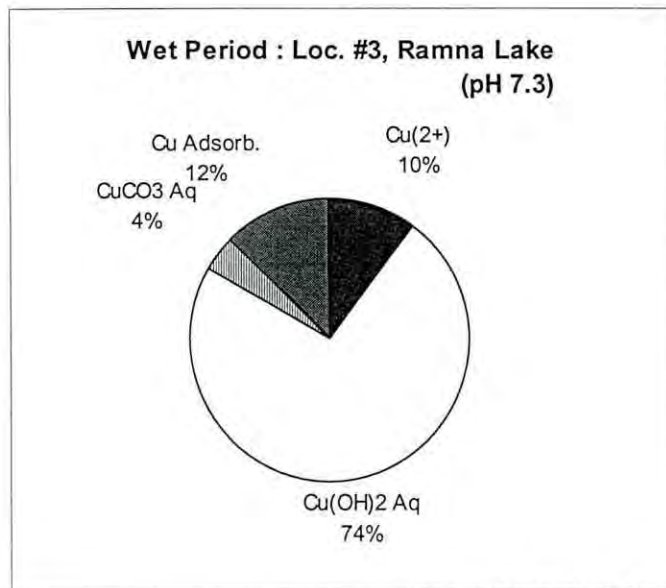
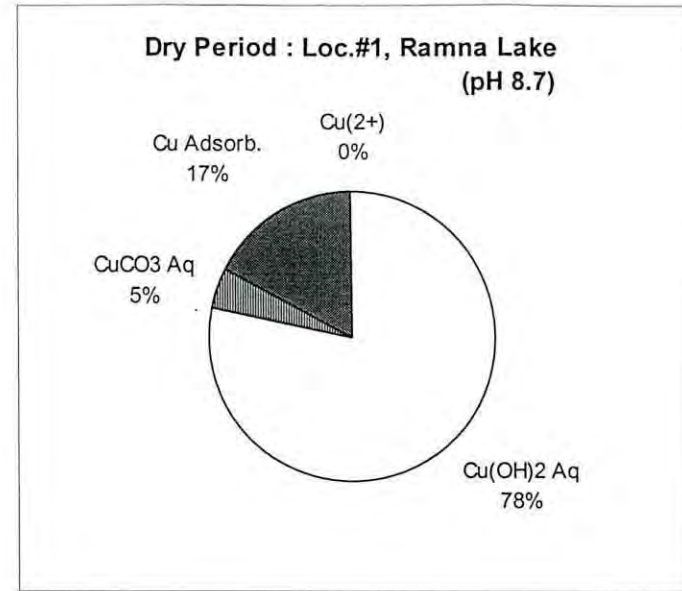
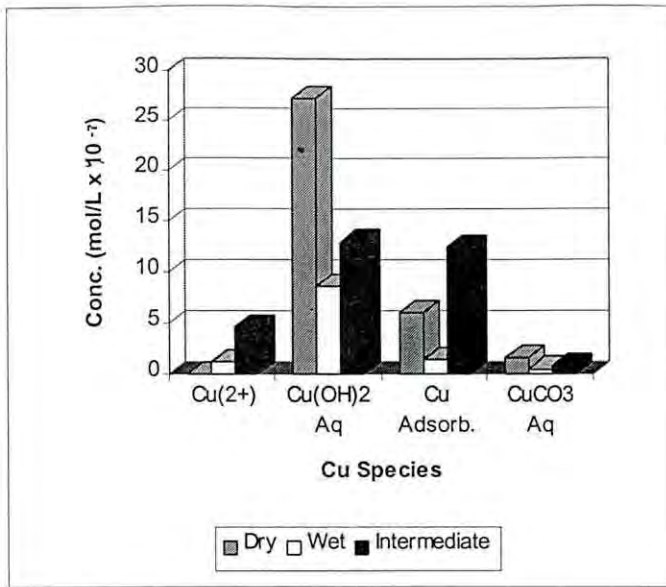


Figure 4.25 : Major Cu species without contribution from sediment (Location 1)

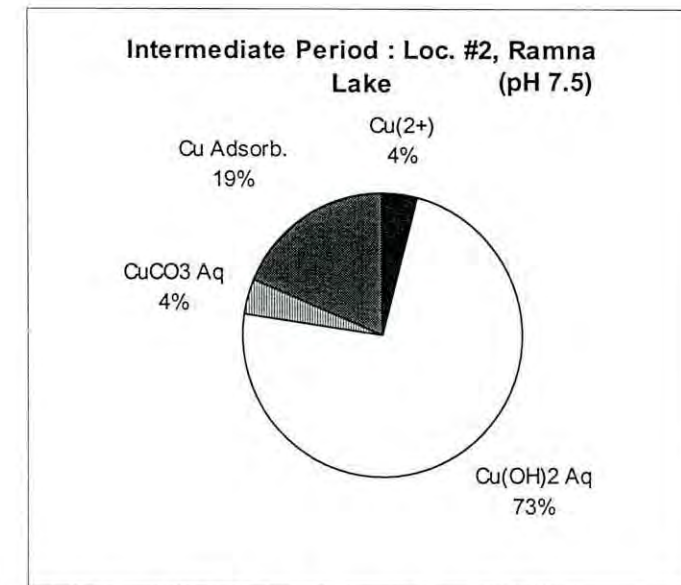
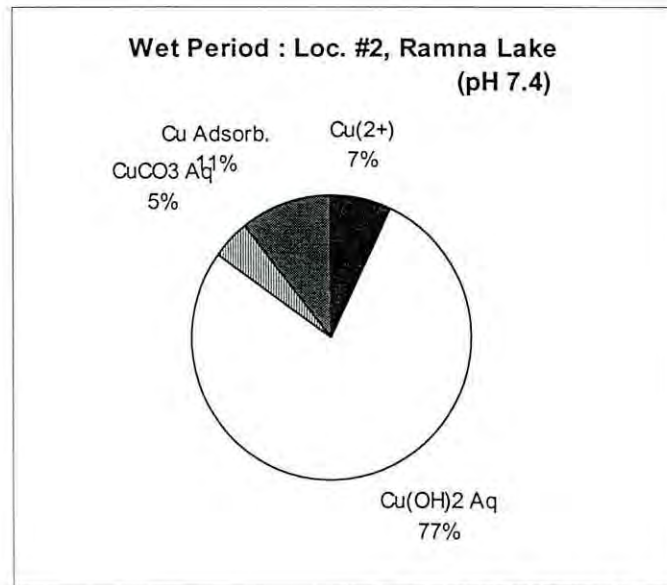
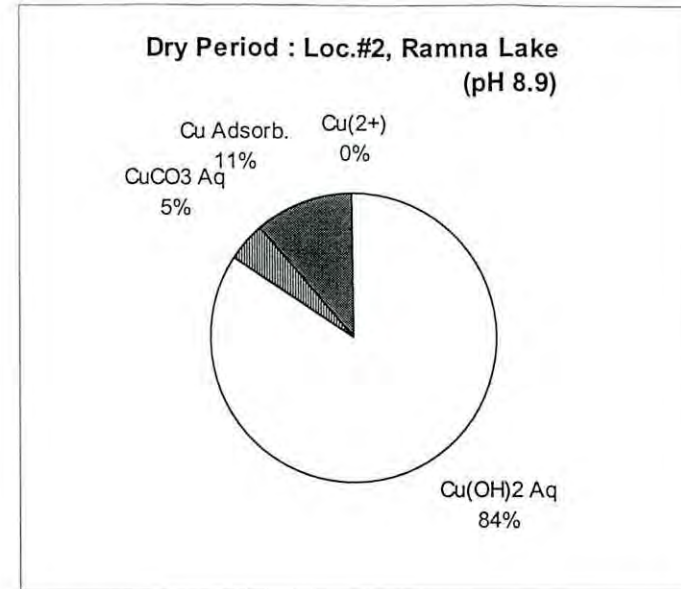
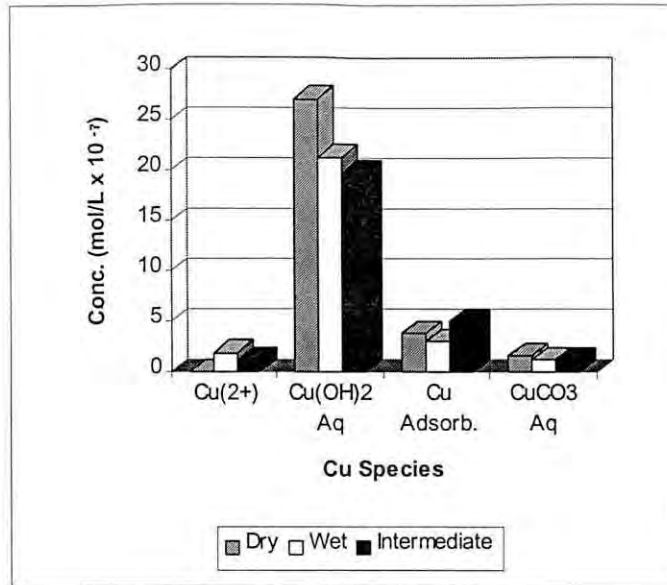


Figure 4.26 : Major Cu species without considering contribution from sediment (Location 2)



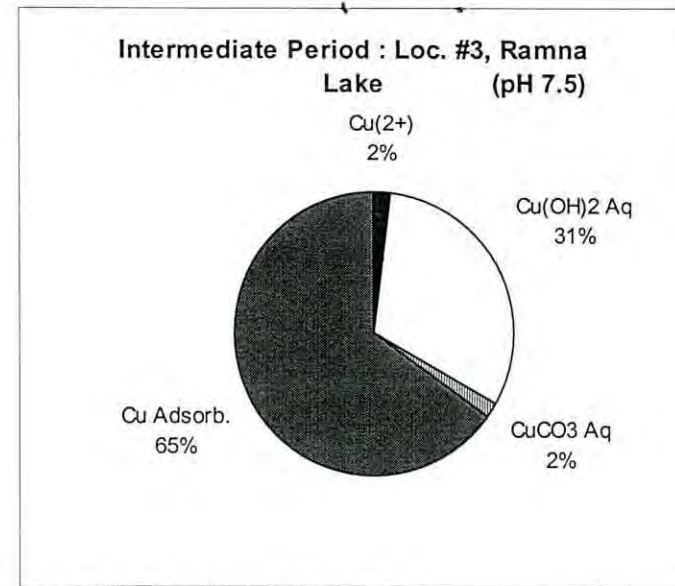
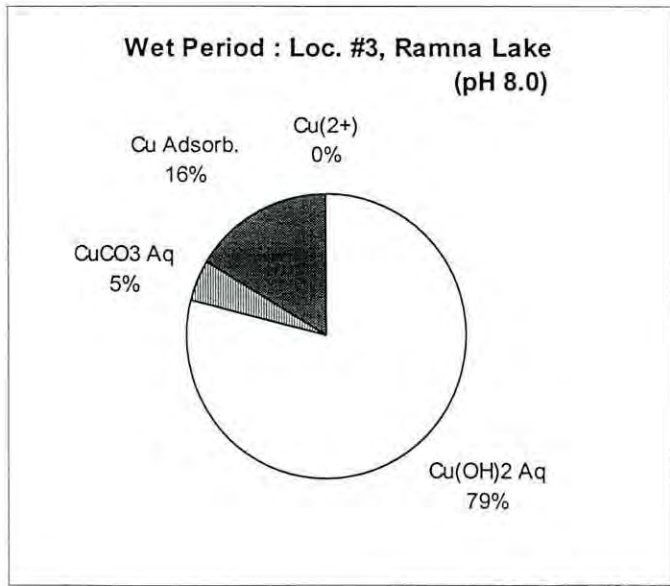
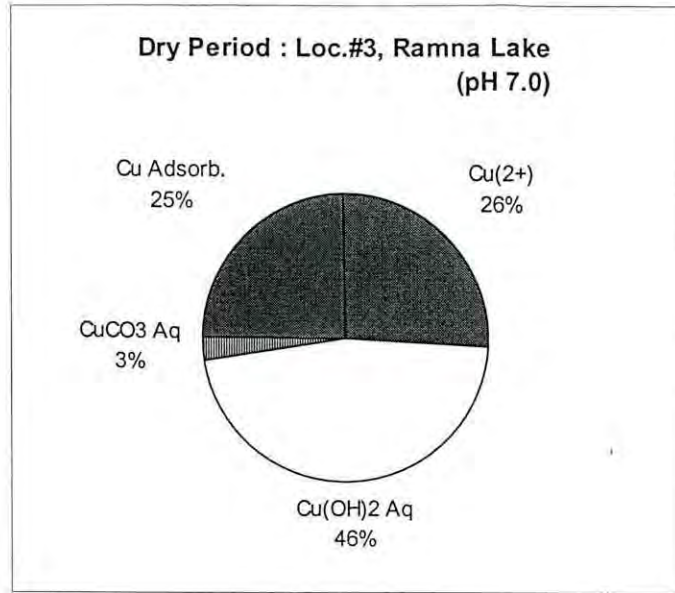
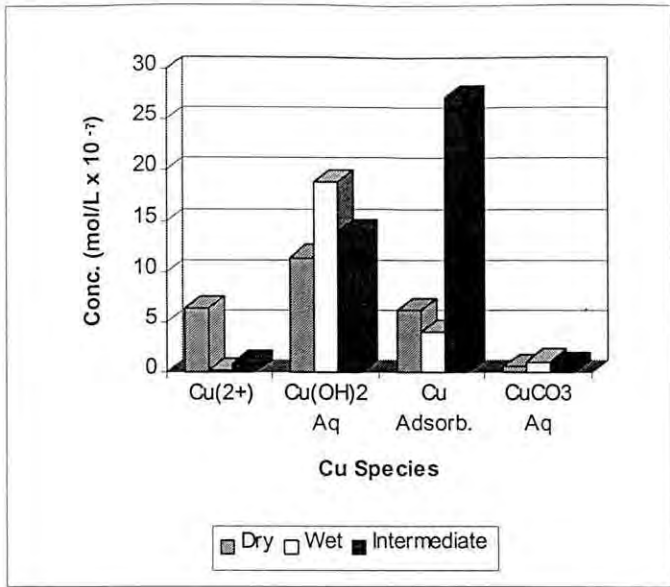


Figure 4.27 : Major Cu species without contribution from sediment (Location 3)

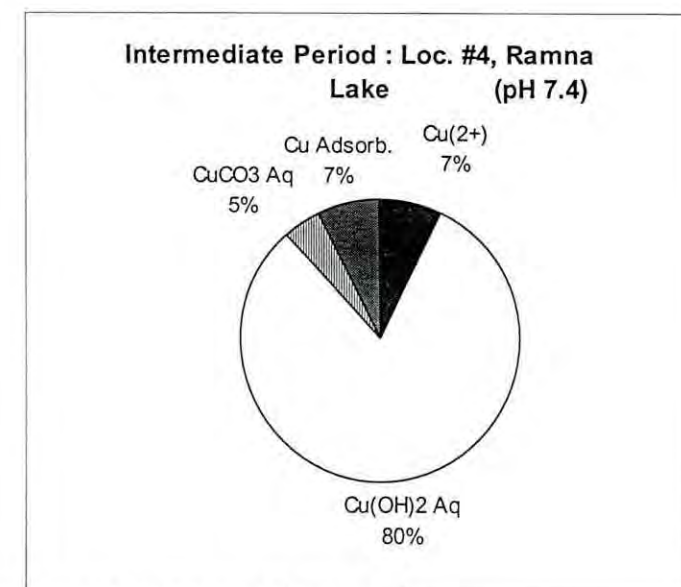
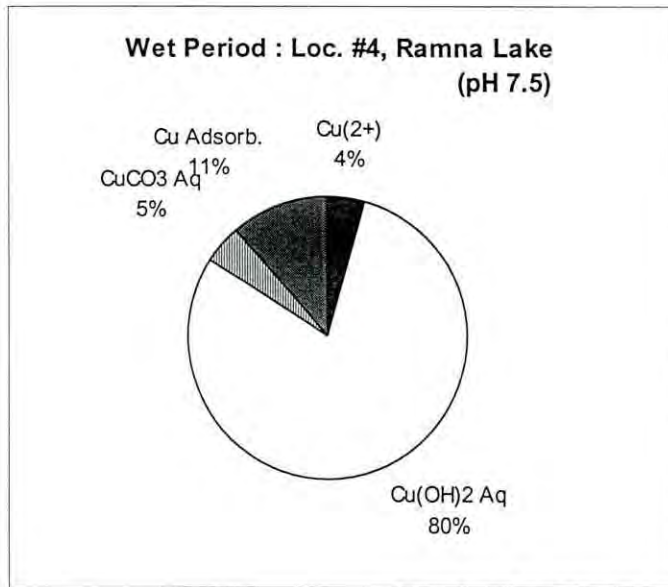
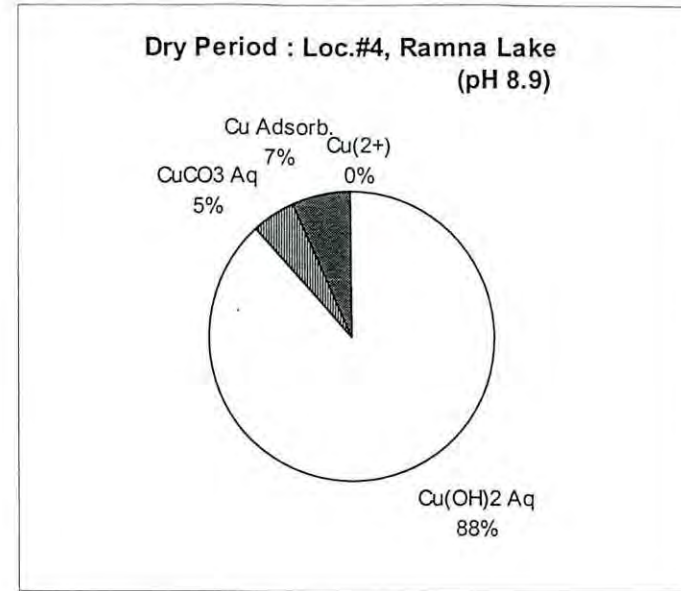
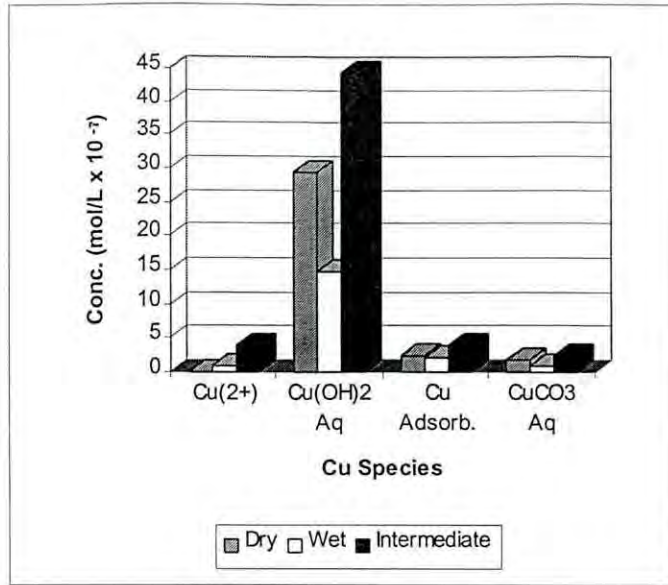


Figure 4.28 : Major Cu species without contribution from sediment (Location 4)

pH at intermediate period was higher than wet period, proportion of  $\text{Cu}^{2+}$  during intermediate was also higher than that during wet period. Deviation from previous findings also occur between wet and intermediate periods for aqueous  $\text{CuCO}_3$  as proportion of aqueous  $\text{CuCO}_3$  was lower during intermediate period than during wet period though pH was higher in dry period. This may be due to error in pH data collection. Concentration of aqueous  $\text{Cu}(\text{OH})_2$  varied from  $2.71 \times 10^{-6}$  to  $1.97 \times 10^{-6}$  mol/l (i.e. 264  $\mu\text{g/l}$  to 192  $\mu\text{g/l}$ ) and  $\text{Cu}^{2+}$  from  $0.189 \times 10^{-6}$  to  $2.38 \times 10^{-10}$  mol/l (i.e. 12  $\mu\text{g/l}$  to 0.02  $\mu\text{g/l}$ ).

Fig. 4.27 shows concentrations of Cu species and their relative proportions (location 3) at three different periods. Concentration of major species aqueous  $\text{Cu}(\text{OH})_2$  was highest in wet period. From the pie chart similar influence of pH on  $\text{Cu}^{2+}$  was evident in lake water. During dry period at lowest pH of 7.0, relative proportion of  $\text{Cu}^{2+}$  was higher than that during other wet period (pH 8.0) and this proportion was lower in wet period than that of intermediate period (pH 7.5). Aqueous  $\text{CuCO}_3$  also follows the trend for dry and wet period. Proportion of aqueous  $\text{CuCO}_3$  in dry period (pH 7.0) was lower than wet period (pH 8.0) and during intermediate period (pH 7.5) the proportion is less than wet period. Concentration of aqueous  $\text{Cu}(\text{OH})_2$  varies from  $2.95 \times 10^{-6}$  to  $1.15 \times 10^{-6}$  mol/l (i.e. 288  $\mu\text{g/l}$  to 112  $\mu\text{g/l}$ ) and  $\text{Cu}^{2+}$  from  $0.646 \times 10^{-6}$  to  $1.06 \times 10^{-8}$  mol/l (i.e. 41  $\mu\text{g/l}$  to 0.67  $\mu\text{g/l}$ ).

Fig 4.28 is for Location 4. Major Cu species aqueous  $\text{Cu}(\text{OH})_2$  was highest during intermediate period. Significant amount of other Cu species  $\text{Cu}^{2+}$ , aqueous  $\text{CuCO}_3$  were observed which showed highest concentrations during intermediate period. From pie chart it is seen that proportion of  $\text{Cu}^{2+}$  increases from dry period (pH 8.9) to wet period (pH 7.5) to intermediate period (pH 7.4) with the decrease in pH. Proportion of aqueous  $\text{CuCO}_3$  remain same in all season though there is a deviation of pH. Concentration of aqueous  $\text{Cu}(\text{OH})_2$  varied from  $4.43 \times 10^{-6}$  to  $1.48 \times 10^{-6}$  mol/l (i.e. 432  $\mu\text{g/l}$  to 144  $\mu\text{g/l}$ ) and  $\text{Cu}^{2+}$  from  $0.396 \times 10^{-6}$  to  $2.59 \times 10^{-10}$  mol/l (i.e. 25  $\mu\text{g/l}$  to 0.02  $\mu\text{g/l}$ ).

Figure 4.29 to 4.31 show spatial and seasonal variation of  $\text{Cu}^{2+}$ , aqueous  $\text{CuCO}_3$  and aqueous  $\text{Cu}(\text{OH})_2$  of the Dhanmondi and Ramna lakes. Aqueous  $\text{CuCO}_3$  and aqueous  $\text{Cu}(\text{OH})_2$  of the Dhanmondi lake show similar pattern. In case of the Ramna lake these aqueous  $\text{CuCO}_3$  and aqueous  $\text{Cu}(\text{OH})_2$  show similar trend.

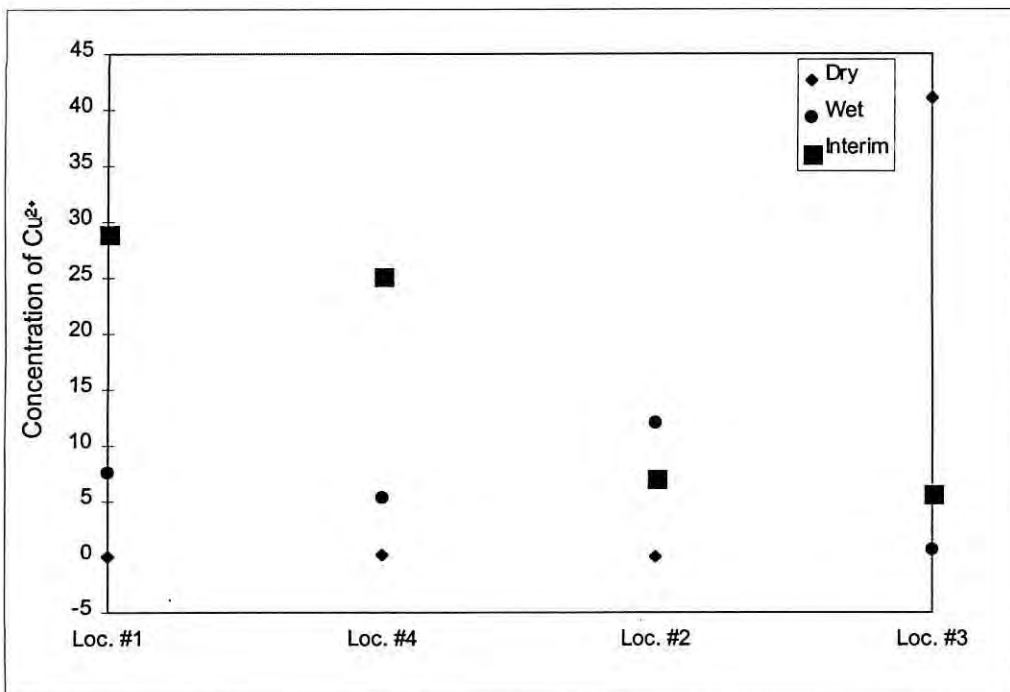
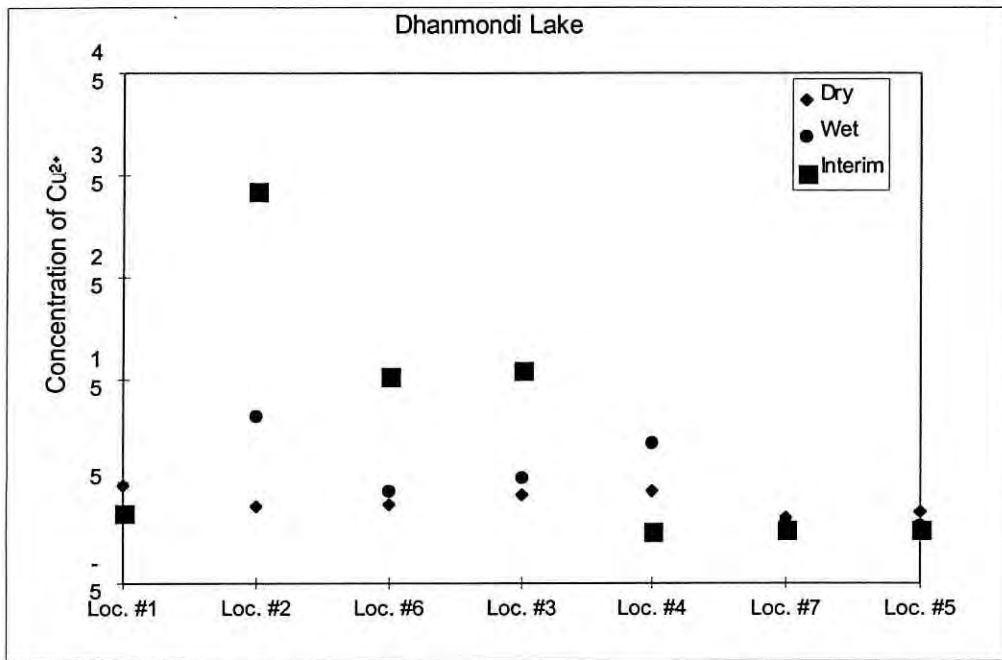


Fig. 4.29 : Spatial and seasonal variation of  $\text{Cu}^{2+}$  (without contribution from sediment)



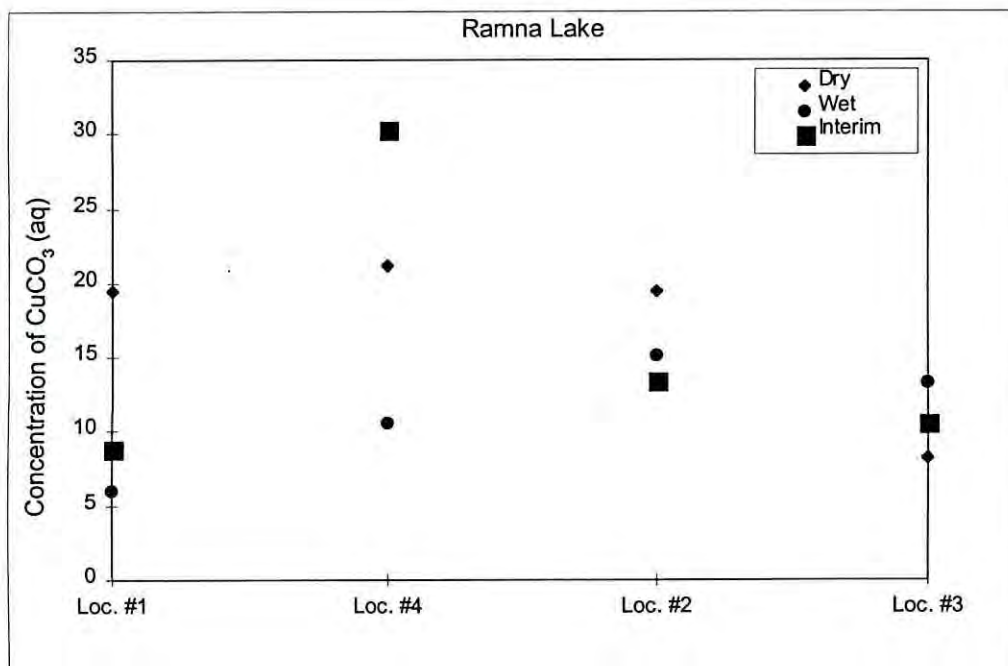
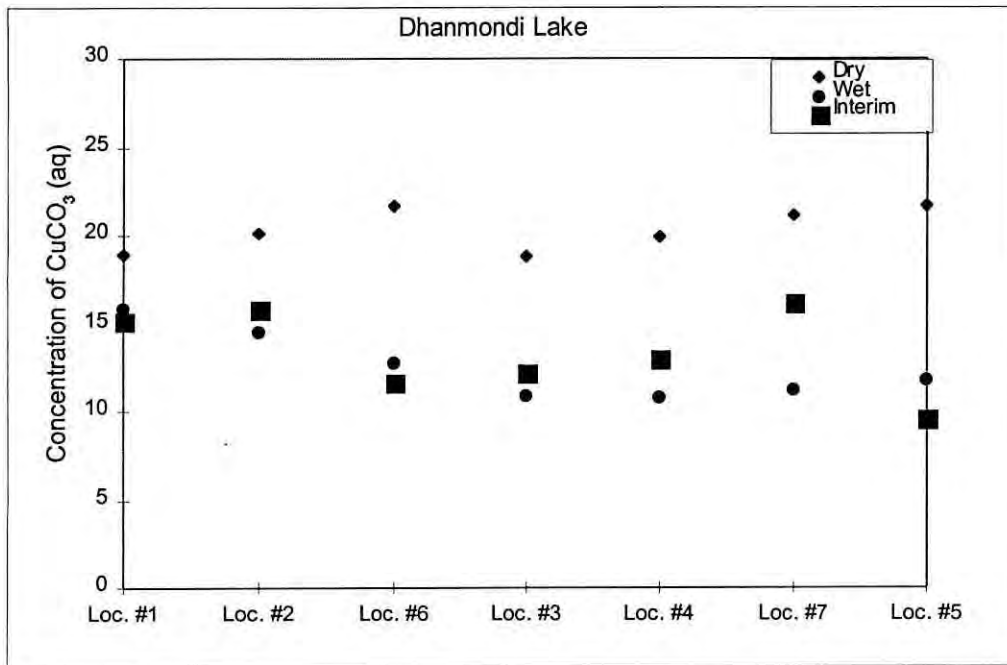


Fig. 4.30 : Spatial and seasonal variation of  $\text{CuCO}_3$  (without contribution from sediment)

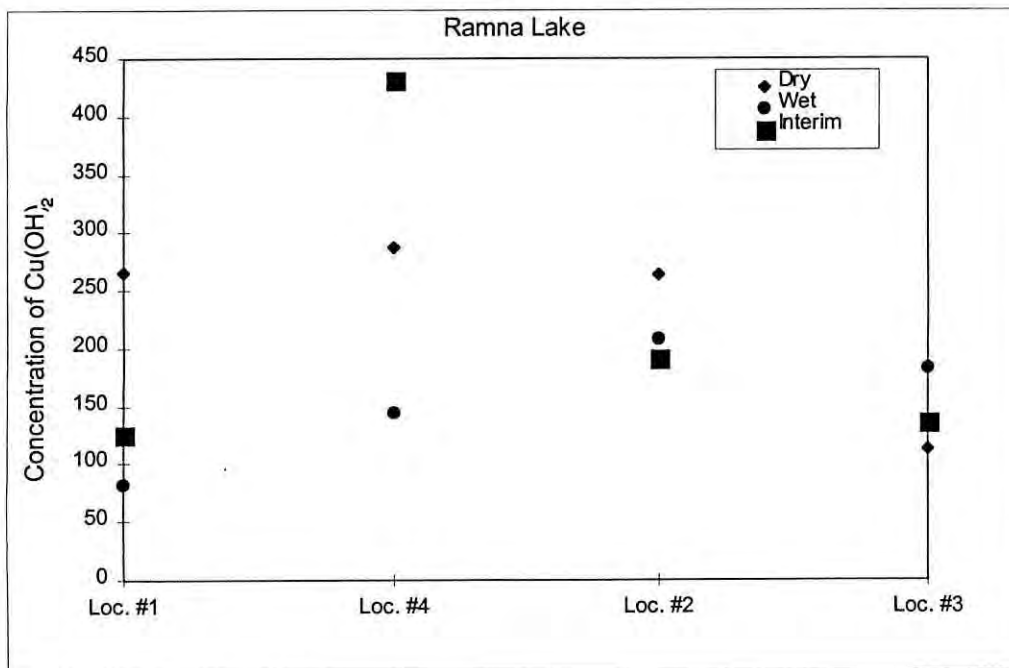
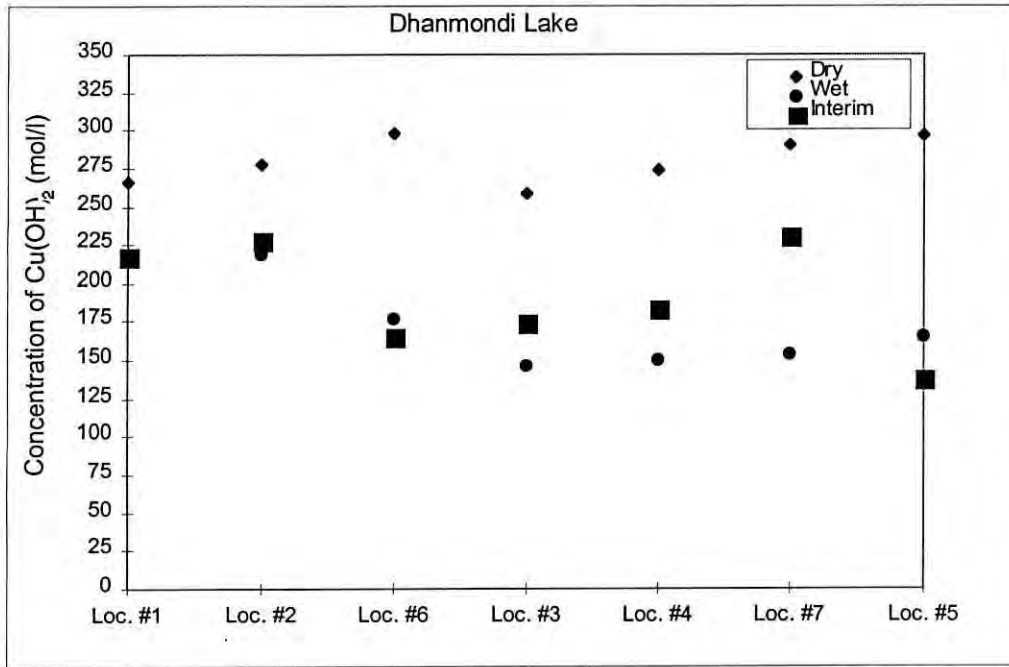


Fig. 4.31 : Spatial and seasonal variation of  $\text{Cu}(\text{OH})_2$  (without contribution from sediment)

### **4.3.2 Speciation of Copper With Considering Contribution From Suspended Sediment**

Equilibrium analysis was also performed for all seven sampling locations of Dhanmondi lake and four sampling locations of Ramna lake considering contribution from sediments. This analysis was also performed to study the effect of exchange at the sediment water interface on the copper distribution in water column. The two layer model described partitioning of copper between aqueous phase and sediment (suspended and bottom sediment). All the outputs are listed in Appendix C.

From Table 4.9, it is found that for both case of the Dhanmondi and Ramna lake concentration of copper adsorbed on suspended sediment is excessively high (92% to 98%). So relative proportion of other copper species were negligible. Only significant copper-species found was aqueous  $\text{Cu}(\text{OH})_2$ .

Comparison of two analyses (e.g. with and without contribution from sediment) indicate that major portion of copper gets adsorbed on suspended sediment and subsequently settle to the bed. It is likely that prolonged deposition of such heavy metals associated with suspended sediment may cause accumulation on the lake-bed. This necessitates an analysis of nature of adsorption of copper depending on the bed particle characteristics. Thus, the present study was extended to analyze the adsorption of copper on particles of different sizes.

### **4.3.3 Conclusions**

A field of campaign followed by equilibrium analysis indicate that water and sediment column of Dhanmondi Lake are heavily contaminated with Cu. But the level of contamination depends very much on the presence of Cu species that are toxic rather than on the total concentration of Cu. Actually, Cu in free form ( $\text{Cu}^{2+}$ ) is more toxic than any other complexed forms. In this analysis, concentration of free Cu in the lake water of Dhanmondi and Ramna lake is not excessively high in general but it is high enough during different periods. In order to determine the toxicity level of copper by determining

Table 4.9 : Adsorption of copper on suspended solids (Considering contribution from sediment)

| Lake      | Location | Percentage of adsorbed copper |      |              |
|-----------|----------|-------------------------------|------|--------------|
|           |          | Dry                           | Wet  | Intermediate |
| Dhanmondi | 1        | 95.6                          | 97.2 | 96.1         |
|           | 2        | 95.9                          | 96.6 | 92.9         |
|           | 3        | 94.9                          | 98.0 | 96.3         |
|           | 4        | 96.4                          | 98.7 | 94.5         |
|           | 5        | 93.8                          | 98.1 | 96.7         |
|           | 6        | 94.3                          | 97.9 | 95.8         |
|           | 7        | 95                            | 97.8 | 93.9         |
| Ramna     | 1        | 95.4                          | 98.7 | 98.7         |
|           | 2        | 94.7                          | 96.1 | 95.7         |
|           | 3        | 98.5                          | 96.5 | 96.7         |
|           | 4        | 95.6                          | 98.3 | 91.5         |



concentrations of various species equilibrium analysis was performed for lake water of Dhanmondi and Ramna Lakes. Equilibrium analysis of water was performed by using a computer program MINEQL<sup>+</sup>. In the equilibrium analysis, two models were considered : The first model was without considering contribution from sediment and only taking suspended sediment and the second was considering contribution from bottom sediment. The major findings for speciation of Cu for all seven sampling locations of Dhanmondi lake and four sampling locations of Ramna lake are :

1. Major Cu species found in equilibrium analysis of the water columns of both the Dhanmondi and the Ramna lakes were  $\text{Cu}(\text{OH})_2 \text{ aq}$ ,  $\text{Cu}^{2+}$ ,  $\text{CuCO}_3 \text{ aq}$ . Concentration of  $\text{Cu}(\text{OH})_2 \text{ aq}$  was found highest of all the Cu species.
2.  $\text{Cu}^{2+}$ , the free form of Cu species and more toxic of any other complexed forms, was also present.
3. From spatial distribution of  $\text{Cu}^{2+}$  it was found that concentration of  $\text{Cu}^{2+}$  is higher on the southern portion of the lake than the northern portion in the Dhanmondi lake.
4. Seasonal variation of  $\text{Cu}^{2+}$  concentration does not show any definite trend.
5. pH is the major controlling factor of Cu speciation. With decrease in pH ionic copper ( $\text{Cu}^{2+}$ ) concentration increases, increasing the toxicity of water as well.
6. Although total copper concentration is very high in lake water toxic form  $\text{Cu}^{2+}$  was not too high but the value increased during some intermediate period for both the Dhanmondi and the Ramna lake.

### 4.3 COPPER CONTAMINATION OF BED SEDIMENT

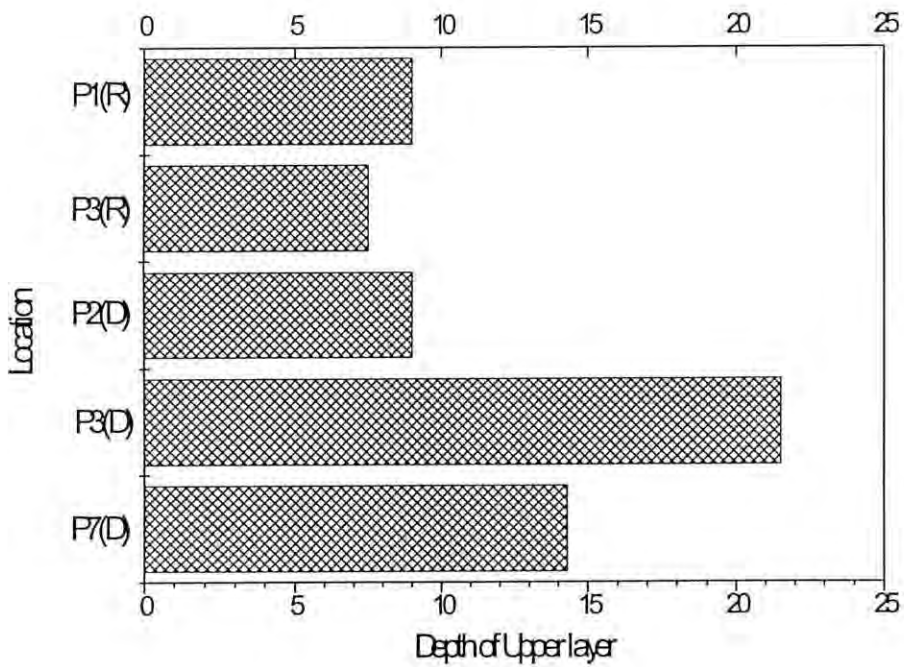
Toxic metals like copper has great affinity for surfaces, which is provided by the solids in suspension and in the bed. Copper is adsorbed on suspended sediment which subsequently settle and accumulate on the bed. Due to sediment water interactions the sediment bed acts as a source of trace metal for biomass. This may occur by settling and resuspension mechanisms of particles between sediment and water column and diffusive exchange between sediment and water column. So analysis of copper in bed sediment is very important for determination of the contamination pattern of whole waterbody.)

Table 4.10 Figure 4.32 shows the depth of top and bottom layer of the sediment column at the time of collection. These sediment samples were collected from locations 2, 3 and 7 of Dhanmondi lake while similar samples were collected from location 1 and 3 of Ramna lake. The sediment columns, each about one foot depth, were divided into two parts depending on the texture. Sediment columns were cut across the line of two distinct colors. It was observed that the top layer was indicating the recent deposition and light colored bottom sediment indicating previous deposits. It was also found that sediment column from Dhanmondi lake is darker than the sediment column of Ramna lake. In Dhanmondi lake depth of upper layer at Location 2 was 9 cm, at location 3 was 21.5 cm and at location 7 was 14.3 cm. In Ramna lake depth of top layer at location 1 was 9 cm while bottom layer was 7.5 cm. From these depths it may assumed that Locations 1 and 3 of Ramna lake and Location 2 of Dhanmondi lake having small depth of top layer sediment receive lesser solids while Location 3 and Location 7 of Dhanmondi have higher deposition. Again from the Table 4.10 and Fig.4.32 it is evident that the depth of upper layer of Locations 1 and 3 of Ramna lake and Location 2 of Dhanmondi are smaller than those of other points which indicate the deposition of these location were older.

Each sediment column divided into two layers (top and bottom), was dried and grounded softly into their smallest particle/grain size by pressing with fingers. Then grains of each layer were subjected to sieve analysis, results of which are shown in Figures 4.33 through 4.42. Fineness Modulus (FM) and Uniformity Coefficient ( $C_u$ ) were determined for each

Table: 4.10 Depth of Upper & Bottom layers of bed sediment columns collected in Dhanmondi and Ramna Lakes:

| Layer Depth      | RAMNA LAKE |      | DHANMONDI LAKE |      |      |
|------------------|------------|------|----------------|------|------|
|                  | P1         | P3   | P2             | P3   | P7   |
| Upper Layer(cm)  | 9          | 7.5  | 9              | 21.5 | 14.3 |
| Bottom Layer(cm) | 14         | 13.5 | 8              | 2.5  | 12.2 |



P represents location points  
 R represents Ramna lake  
 D represents Dhanmondi lake

Figure: 4.32 Depth of top layer of sediment column of Dhanmondi and Ramna lakes

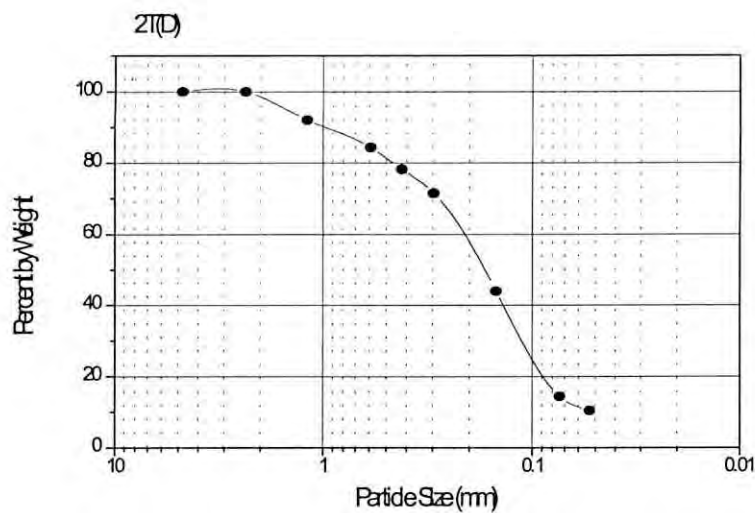
sample. For Dhanmondi lake FM ranged from 1.0 to 2.0 and Uniformity coefficient (Cu) ranges from 1 to 4. However, in case of Ramna lake these values ranged from 1.0 to 3.0 and from 4.0 to 11.0 respectively. From these values it is evident that the sediment particles of the Ramna lake were relatively coarser than those of Dhanmondi lake. In most cases the major portions of the sediment particles of both the lakes were retained on sieve #100 (0.149 mm) and sieve #200 (0.074 mm). Thus the major portion of particle ranged between 0.297 mm to 0.074 mm.

After grain size analysis, portion of sediment samples retained on different sieves were digested. Concentration of copper adsorbed on each size of the particle was determined by Atomic Adsorption Spectrophotometer which is shown in table 4.11. These values are graphically represented in Fig. 4.43 to 4.47. These figures show adsorptions of copper on different size of the particles at each location of the Dhanmondi lake and the Ramna lake. Concentration of copper adsorbed on particles retained on sieve #40 (i.e. ranging from 0.42 mm to 0.59 mm) of location 2 was relatively higher than those of the other locations of Dhanmondi lake. In Ramna lake concentration of copper adsorbed on particles of Location 1 was relatively higher than that of Location 3. In Ramna lake at Location 1, it can be observed that top layer sediment contains more copper in adsorbed form than bottom layer. However, no such trends could be found from other locations.

Table 4.11 and Figures 4.43 and 4.44 show copper adsorbed on particles size within a definite range at different locations of Ramna and Dhanmondi lakes. From these figures it can be observed that maximum amount of copper was adsorbed on particles ranging from 0.42 mm to 0.59mm.



| Sieve No. | Sieve Size (mm) | Material retained (gm) | Percent material retained | Cumulative percent retained | Percent finer |
|-----------|-----------------|------------------------|---------------------------|-----------------------------|---------------|
| No. 4     | 4.76            | 0                      | 0                         | 0                           | 100           |
| No. 8     | 2.38            | 0                      | 0                         | 0                           | 100           |
| No. 16    | 1.19            | 4                      | 8                         | 8                           | 92            |
| No. 30    | 0.59            | 3.9                    | 7.8                       | 15.8                        | 84.2          |
| No. 40    | 0.42            | 3                      | 6                         | 21.8                        | 78.2          |
| No. 50    | 0.297           | 3.3                    | 6.6                       | 28.6                        | 71.4          |
| No. 100   | 0.149           | 13.8                   | 27.6                      | 56.0                        | 44            |
| No. 200   | 0.074           | 14.8                   | 29.6                      | 85.6                        | 14.4          |
| No. 270   | 0.053           | 2                      | 4                         | 89.6                        | 10.4          |
| Pan       |                 | 5.2                    | 10.4                      | 100                         | 0             |

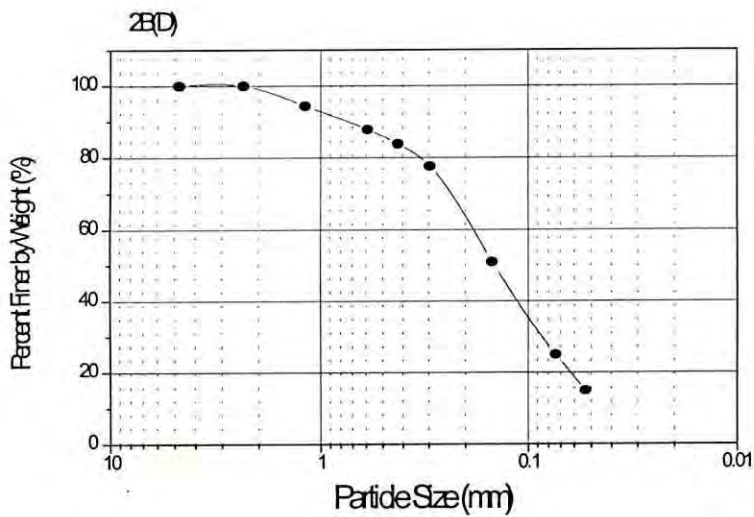


**Fineness Modulus (FM) = 1.084**

**Uniformity Coefficient ( $C_u$ ) = 3.82**

Fig. 4.33 : Grain Size distribution of top layer sediment at location 2 of Dhanmondi Lake

| Sieve No. | Sieve Size (mm) | Material retained (gm) | Percent Material retained | Cumulative percent retained | Percent finer |
|-----------|-----------------|------------------------|---------------------------|-----------------------------|---------------|
| No. 4     | 4.76            | 0                      | 0                         | 0                           | 100           |
| No. 8     | 2.38            | 0                      | 0                         | 0                           | 100           |
| No. 16    | 1.19            | 2.8                    | 5.6                       | 5.6                         | 94.4          |
| No. 30    | 0.59            | 3.3                    | 6.6                       | 12.2                        | 87.8          |
| No. 40    | 0.42            | 2                      | 4                         | 16.2                        | 83.8          |
| No. 50    | 0.297           | 3.1                    | 6.2                       | 22.4                        | 77.6          |
| No. 100   | 0.149           | 13.3                   | 26.6                      | 49                          | 51            |
| No. 200   | 0.074           | 13                     | 26                        | 75                          | 25            |
| No. 270   | 0.053           | 5.0                    | 10.0                      | 85                          | 15            |
| Pan       |                 | 7.5                    | 15.0                      | 100                         | 0             |

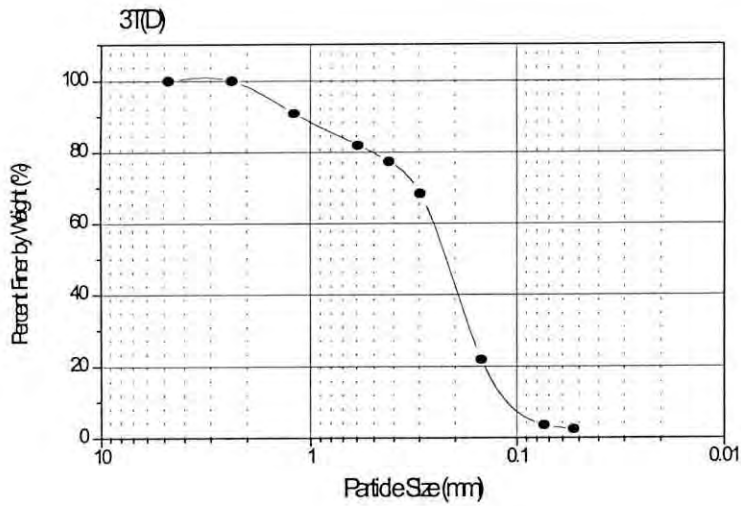


**Fineness Modulus (FM) = 0.892**

**Uniformity Coefficient ( $C_u$ ) = 4.0**

Fig. 4.34: Sieve analysis of bottom sediment at location 2 of Dhanmondi Lake

| Sieve No. | Sieve Size (mm) | Material retained (gm) | Percent Material retained | Cumulative percent retained | Percent finer |
|-----------|-----------------|------------------------|---------------------------|-----------------------------|---------------|
| No. 4     | 4.76            | 0                      | 0                         | 0                           | 100           |
| No. 8     | 2.38            | 0                      | 0                         | 0                           | 100           |
| No. 16    | 1.19            | 9.1                    | 9.1                       | 9.1                         | 90.9          |
| No. 30    | .59             | 9.0                    | 9.0                       | 18.1                        | 81.9          |
| No. 40    | .42             | 4.5                    | 4.5                       | 22.6                        | 77.4          |
| No. 50    | .297            | 9.0                    | 9.0                       | 31.6                        | 68.4          |
| No. 100   | .149            | 46.7                   | 46.7                      | 78.1                        | 21.9          |
| No. 200   | .074            | 18.2                   | 18.2                      | 96.3                        | 3.7           |
| No. 270   | .053            | 1.2                    | 1.2                       | 97.5                        | 2.5           |
| Pan       |                 | 2.5                    | 2.5                       | 100                         | 0             |

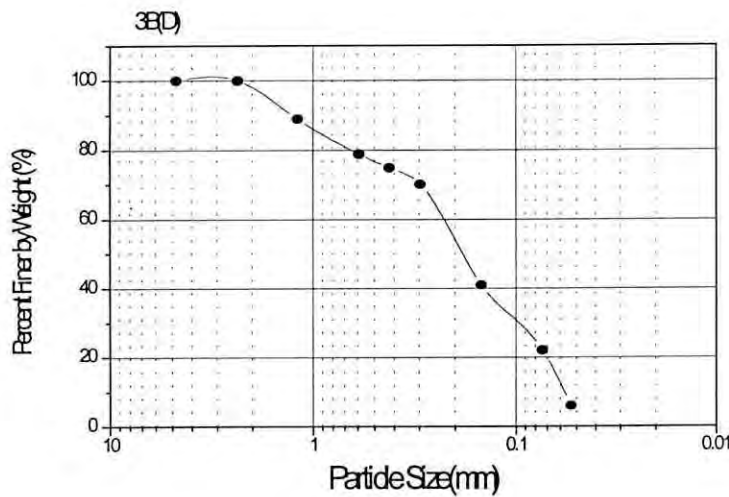


Fineness Modulus (FM) = 1.084

Uniformity Coefficient ( $C_u$ ) = 3.82

Fig. 4.35 : Grain Size distribution of top layer sediment at Location 3 of Dhanmondi Lake

| Sieve No. | Sieve Size (mm) | Material retained (gm) | Percent Material retained | Cumulative percent retained | Percent finer |
|-----------|-----------------|------------------------|---------------------------|-----------------------------|---------------|
| No. 4     | 4.76            | 0                      | 0                         | 0                           | 100           |
| No. 8     | 2.38            | 0                      | 0                         | 0                           | 100           |
| No. 16    | 1.19            | 5.5                    | 11.0                      | 11.0                        | 89            |
| No. 30    | 0.59            | 5.1                    | 10.2                      | 21.2                        | 78.8          |
| No. 40    | 0.42            | 2.0                    | 4.0                       | 25.2                        | 74.8          |
| No. 50    | 0.297           | 2.4                    | 4.8                       | 30.0                        | 70.0          |
| No. 100   | 0.149           | 14.5                   | 29.0                      | 59.0                        | 41.0          |
| No. 200   | 0.074           | 14.5                   | 29.0                      | 88.0                        | 22.0          |
| No. 270   | 0.053           | 3                      | 6                         | 94.0                        | 6.0           |
| Pan       |                 | 3                      | 6                         | 100.0                       | 0             |



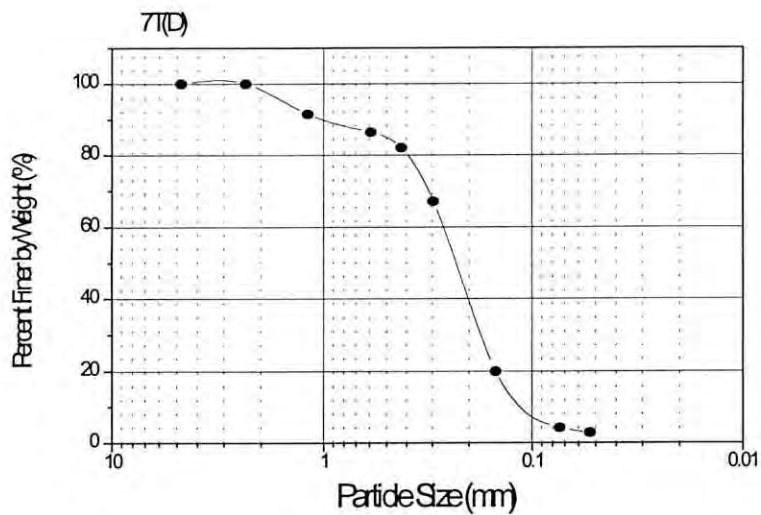
Fineness Modulus (FM) = 1.212

Uniformity Coefficient ( $C_u$ ) = 0.932

Fig. 4.36: Grain Size distribution of bottom layer sediment at location 3 of Dhanmondi lake



| Sieve No. | Sieve Size (mm) | Material retained (gm) | Percent material retained | Cumulative percent retained | Percent finer |
|-----------|-----------------|------------------------|---------------------------|-----------------------------|---------------|
| No. 4     | 4.76            | 0                      | 0                         | 0                           | 100           |
| No. 8     | 2.38            | 0                      | 0                         | 0                           | 100           |
| No. 16    | 1.19            | 8.5                    | 8.5                       | 8.5                         | 91.5          |
| No. 30    | .59             | 5.0                    | 5.0                       | 13.5                        | 86.5          |
| No. 40    | .42             | 4.5                    | 4.5                       | 18.0                        | 82.0          |
| No. 50    | .297            | 15                     | 15                        | 33.0                        | 67            |
| No. 100   | .149            | 47.2                   | 47.2                      | 80.2                        | 19.8          |
| No. 200   | .074            | 15.5                   | 15.5                      | 95.7                        | 4.3           |
| No. 270   | .053            | 1.5                    | 1.5                       | 97.2                        | 2.8           |
| Pan       |                 | 2.8                    | 2.8                       | 100                         | 0             |

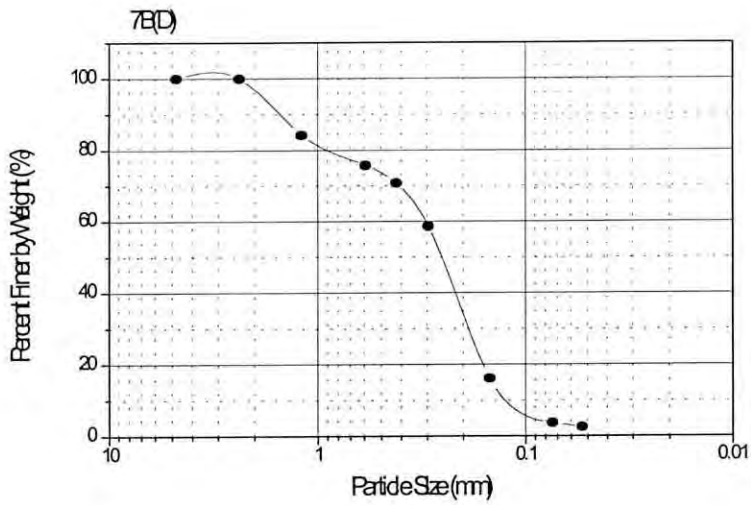


Fineness Modulus (FM) = 1.352

Uniformity Coefficient ( $C_u$ ) = 2.36

Fig. 4.37: Grain Size distribution of top layer sediment at location 7 of Dhanmondi lake

| Sieve No. | Sieve Size (mm) | Material retained (gm) | Percent Material retained | Cumulative percent retained | Percent finer |
|-----------|-----------------|------------------------|---------------------------|-----------------------------|---------------|
| No. 4     | 4.76            | 0                      | 0                         | 0                           | 0             |
| No. 8     | 2.38            | 0                      | 0                         | 0                           | 0             |
| No. 16    | 1.19            | 15.8                   | 15.8                      | 15.8                        | 84.2          |
| No. 30    | .59             | 8.5                    | 8.5                       | 24.3                        | 75.7          |
| No. 40    | .42             | 5.0                    | 5.0                       | 29.3                        | 70.7          |
| No. 50    | .297            | 12.0                   | 12.0                      | 41.3                        | 58.7          |
| No. 100   | .149            | 42.5                   | 42.5                      | 83.8                        | 16.2          |
| No. 200   | .074            | 12.5                   | 12.5                      | 96.3                        | 3.7           |
| No. 270   | .053            | 1.2                    | 1.2                       | 97.5                        | 2.5           |
| Pan       |                 | 2.5                    | 2.5                       | 100                         | 0             |

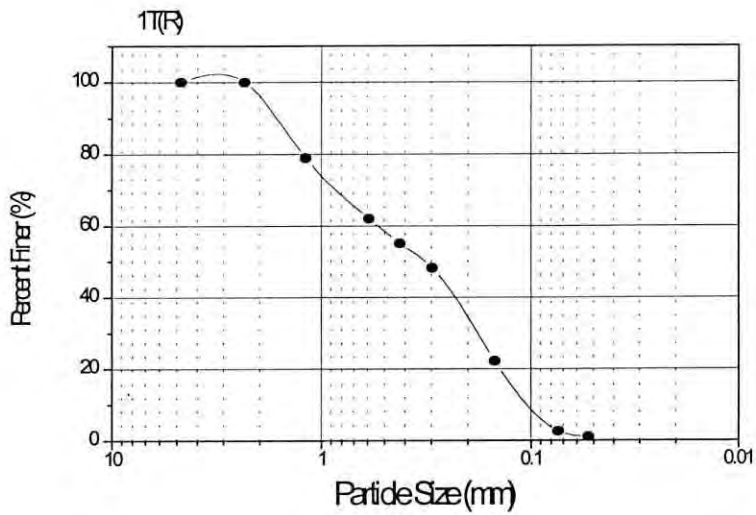


**Fineness Modulus (FM) = 1.652**

**Uniformity Coefficient ( $C_u$ ) = 2.5**

Fig. 4.38: Grain Size distribution of bottom layer sediment at location 7 of Dhanmondi Lake

| Sieve No. | Sieve Size (mm) | Material retained (gm) | Percent Material retained | Cumulative percent retained | Percent finer |
|-----------|-----------------|------------------------|---------------------------|-----------------------------|---------------|
| No. 4     | 4.76            | 0                      | 0                         | 0                           | 100           |
| No. 8     | 2.38            | 0                      | 0                         | 0                           | 100           |
| No. 16    | 1.19            | 10.5                   | 21                        | 21                          | 79            |
| No. 30    | 0.59            | 8.5                    | 17                        | 38                          | 62            |
| No. 40    | 0.42            | 3.4                    | 6.8                       | 44.8                        | 55.2          |
| No. 50    | 0.297           | 3.5                    | 7                         | 51.8                        | 48.2          |
| No. 100   | 0.149           | 13                     | 26                        | 77.8                        | 22.22         |
| No. 200   | 0.074           | 9.8                    | 19.6                      | 97.4                        | 2.6           |
| No. 270   | 0.053           | 0.8                    | 1.6                       | 99                          | 1             |
| Pan       |                 | 0.5                    | 1.0                       | 0                           | 0             |

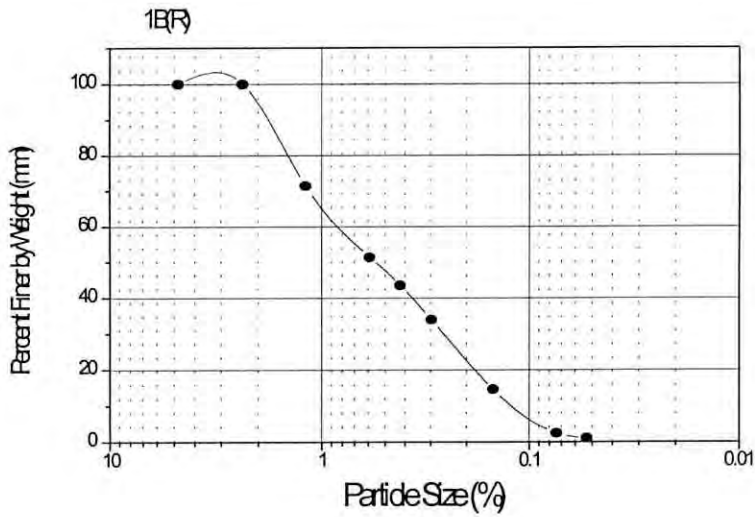


Fineness Modulus (FM) = 1.886

Uniformity Coefficient ( $C_u$ ) = 4.09

Fig. 4.39 : Grain Size distribution of top sediment at location 1 of Ramna Lake

| Sieve No: | Sieve Size (mm) | Material retained (gm) | Percent Material retained | Cumulative percent retained | Percent finer |
|-----------|-----------------|------------------------|---------------------------|-----------------------------|---------------|
| No. 4     | 4.76            | 0                      | 0                         | 0                           | 0             |
| No. 8     | 2.38            | 0                      | 0                         | 0                           | 0             |
| No. 16    | 1.19            | 28.5                   | 28.5                      | 28.5                        | 71.5          |
| No. 30    | .59             | 20                     | 20.0                      | 48.5                        | 51.5          |
| No. 40    | .42             | 8.0                    | 8.0                       | 56.5                        | 43.5          |
| No. 50    | .297            | 9.5                    | 9.5                       | 66.0                        | 34.0          |
| No. 100   | .149            | 19.5                   | 19.5                      | 85.5                        | 14.5          |
| No. 200   | .074            | 12                     | 12                        | 97.5                        | 2.5           |
| No. 270   | .053            | 1.5                    | 1.5                       | 99.0                        | 1.0           |
| Pan       |                 | 1.0                    | 1.0                       | 100                         |               |



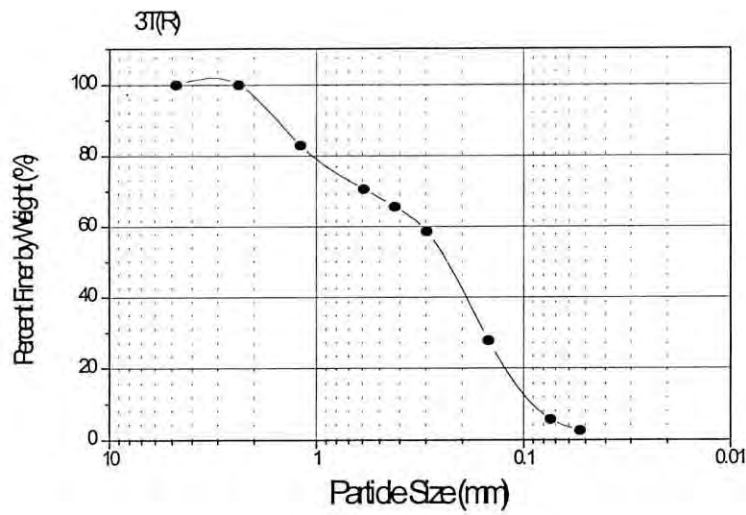
Fineness Modulus (FM) = 2.285

Uniformity Coefficient ( $C_u$ ) = 6.8

Fig. 4.40: Grain Size distribution of bottom layer sediment at location 1 of Ramna Lake



| Sieve No. | Sieve Size (mm) | Material retained (gm) | Percent Material retained | Cumulative percent retained | Percent finer |
|-----------|-----------------|------------------------|---------------------------|-----------------------------|---------------|
| No. 4     | 4.76            | 0                      | 0                         | 0                           | 100           |
| No. 8     | 2.38            | 0                      | 0                         | 0                           | 100           |
| No. 16    | 1.19            | 8.5                    | 17                        | 17                          | 83            |
| No. 30    | 0.59            | 6.2                    | 12.4                      | 29.4                        | 70.6          |
| No. 40    | 0.42            | 2.5                    | 5                         | 34.4                        | 65.6          |
| No. 50    | 0.297           | 3.7                    | 7.4                       | 41.8                        | 58.5          |
| No. 100   | 0.149           | 15.2                   | 30.4                      | 72.2                        | 27.8          |
| No. 200   | 0.074           | 11                     | 22                        | 94.2                        | 5.8           |
| No. 270   | 0.053           | 1.6                    | 3.2                       | 97.4                        | 2.6           |
| Pan       |                 | 1.3                    | 2.6                       |                             |               |

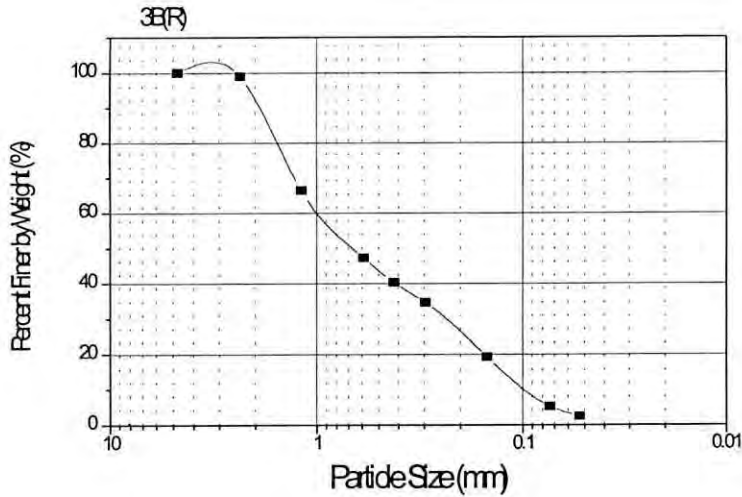


**Fineness Modulus (FM) = 1.604**

**Uniformity Coefficient ( $C_u$ ) = 2.23**

Fig. 4.41: Grain Size distribution of top layer sediment at location 3 of Ramna Lake

| Sieve No. | Sieve Size (mm) | Material retained (gm) | Percent Material retained | Cumulative percent retained | Percent finer |
|-----------|-----------------|------------------------|---------------------------|-----------------------------|---------------|
| No. 4     | 4.76            | 0                      | 0                         | 0                           | 100           |
| No. 8     | 2.38            | 1                      | 1                         | 1                           | 99            |
| No. 16    | 1.19            | 32.5                   | 32.5                      | 33.5                        | 66.5          |
| No. 30    | 0.59            | 19.2                   | 19.2                      | 52.7                        | 47.3          |
| No. 40    | 0.42            | 7                      | 7                         | 59.7                        | 40.3          |
| No. 50    | 0.297           | 5.6                    | 5.6                       | 65.3                        | 34.7          |
| No. 100   | 0.149           | 15.4                   | 15.4                      | 80.7                        | 19.3          |
| No. 200   | 0.074           | 14                     | 14                        | 94.7                        | 5.3           |
| No. 270   | 0.053           | 2.8                    | 2.8                       | 97.5                        | 2.5           |
| Pan       |                 | 2.5                    | 2.5                       |                             |               |



Fineness Modulus (FM) = 2.33

Uniformity Coefficient ( $C_u$ ) = 10.10

Fig. 4.42 : Grain Size distribution of bottom layer sediment at location 3 of Ramna Lake

Table 4.11: Copper adsorbed (mg/kg) on different grain size at differnt layers at different points in Dhanmondi & Ramna lake

| Sieve No         | RAMNA LAKE |           |           |           | DHANMONDI LAKE |           |           |           |           |           |
|------------------|------------|-----------|-----------|-----------|----------------|-----------|-----------|-----------|-----------|-----------|
|                  | 1T<br>(R)  | 1B<br>(R) | 3T<br>(R) | 3B<br>(R) | 2T<br>(D)      | 2B<br>(D) | 3T<br>(D) | 3B<br>(D) | 7T<br>(D) | 7B<br>(D) |
| # 16             | 34.39      | 31.97     | 29.65     | 17.31     | 42.41          | 48.33     | 28.39     | 12.77     | 15.95     | 29.80     |
| # 30             | 40.10      | 32.80     | 23.41     | 31.35     | 49.49          | 25.29     | 17.88     | 42.80     | 26.86     | 26.20     |
| # 40             | 46.98      | 40.62     | 47.77     | 46.21     | 59.45          | 49.13     | 32.25     | 52.28     | 27.20     | 34.28     |
| # 50             | 44.15      | 33.95     | 32.75     | 45.12     | 42.85          | 25.43     | 21.59     | 30.05     | 22.35     | 31.28     |
| # 100            | 33.94      | 32.88     | 29.61     | 30.16     | 38.75          | 34.73     | 17.75     | 10.55     | 10.83     | 24.99     |
| # 200            | 42.99      | 41.74     | 43.72     | 46.44     | 38.14          | 45.46     | -         | -         | 18.74     | 29.07     |
| Weighted<br>Avg. | 38.57      | 34.39     | 33.38     | 30.47     | 41.61          | 38.67     | 20.28     | 20.96     | 15.98     | 27.67     |

\* B represents Bottom sediment layers

\* R represents Ramna Lake

\* T represents Top sediment layers

\* D represents Dhanmondi Lake

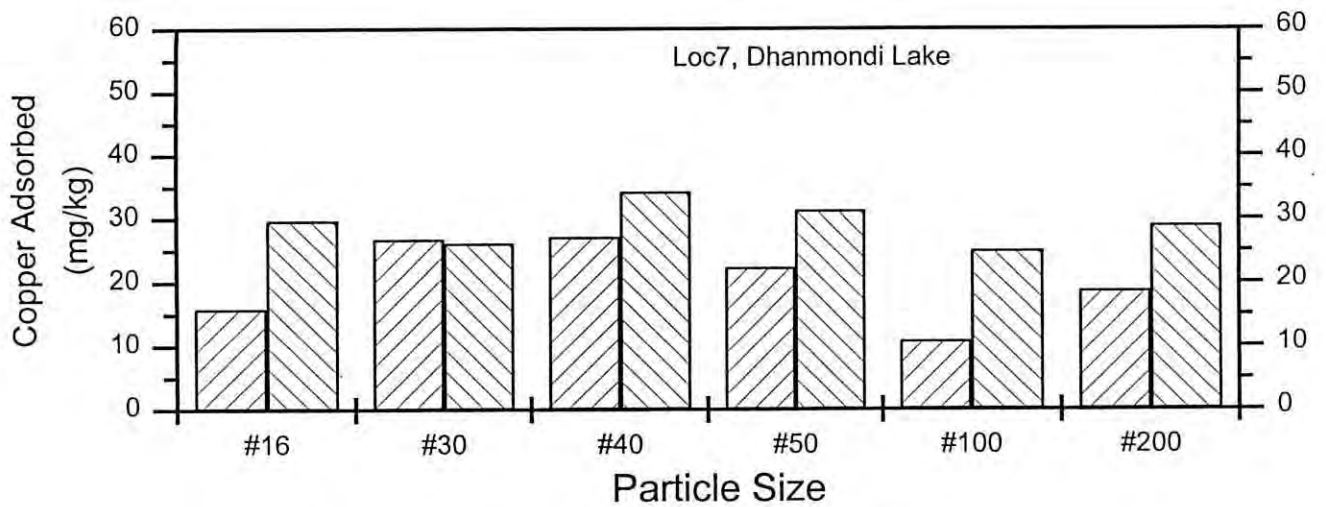
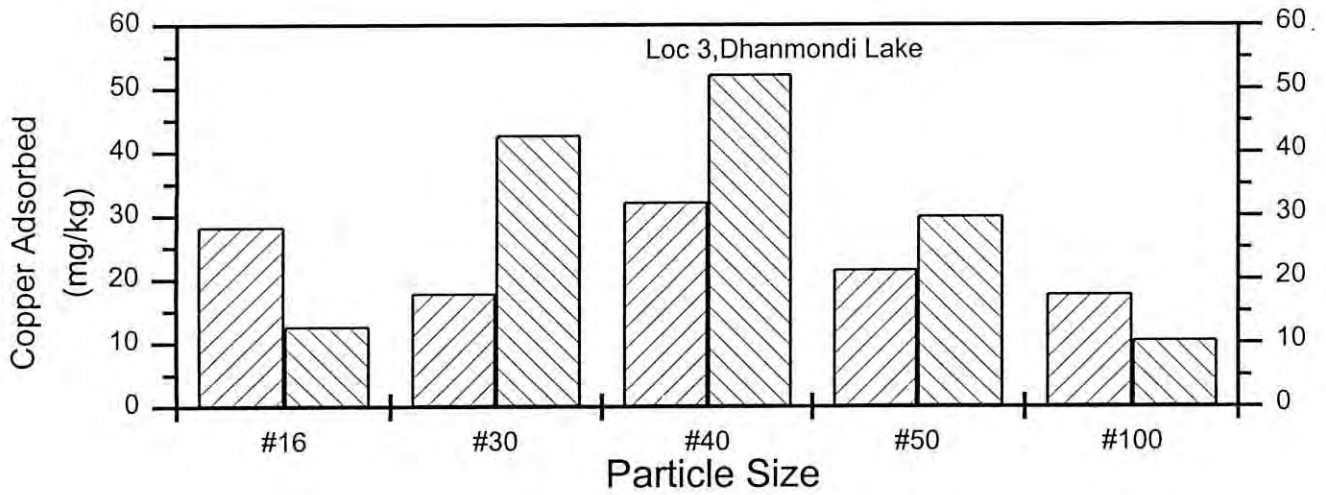
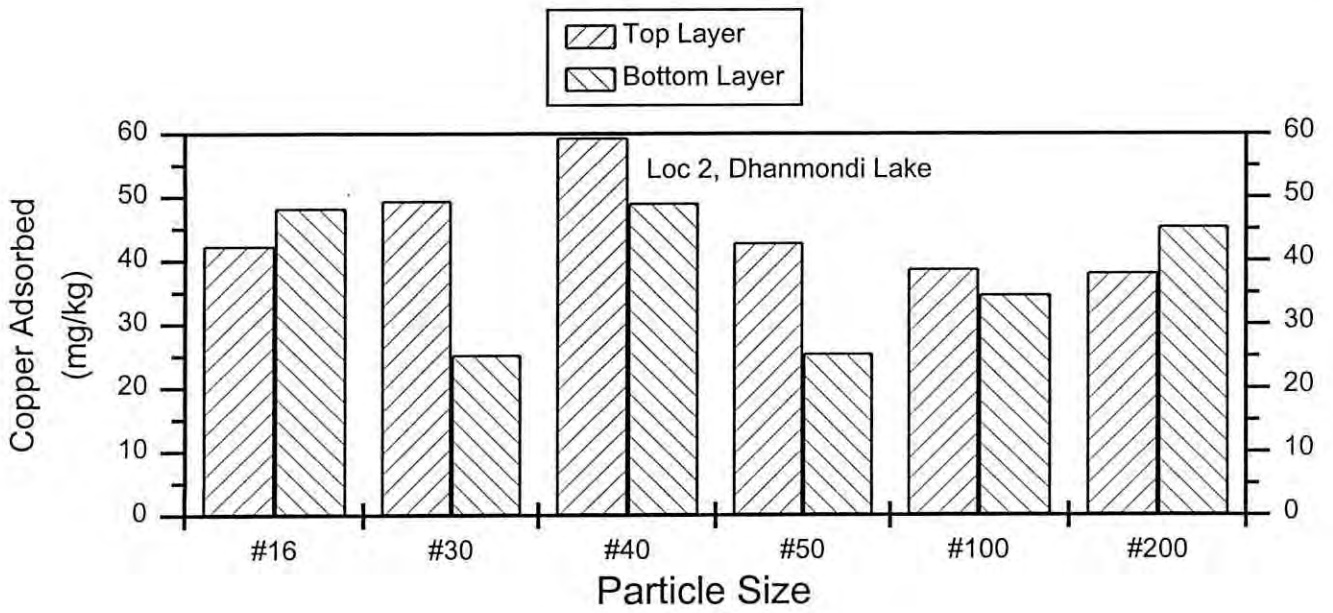


Fig.4.43 : Copper Adsorption on Different Size of Particles



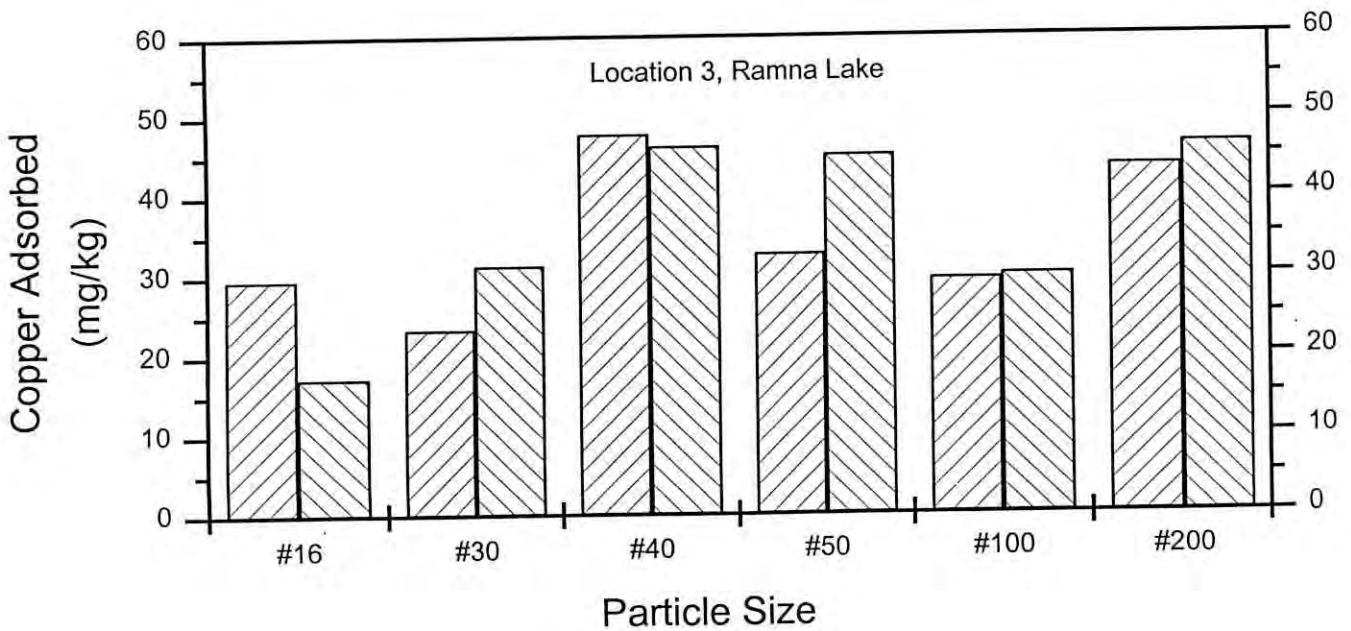
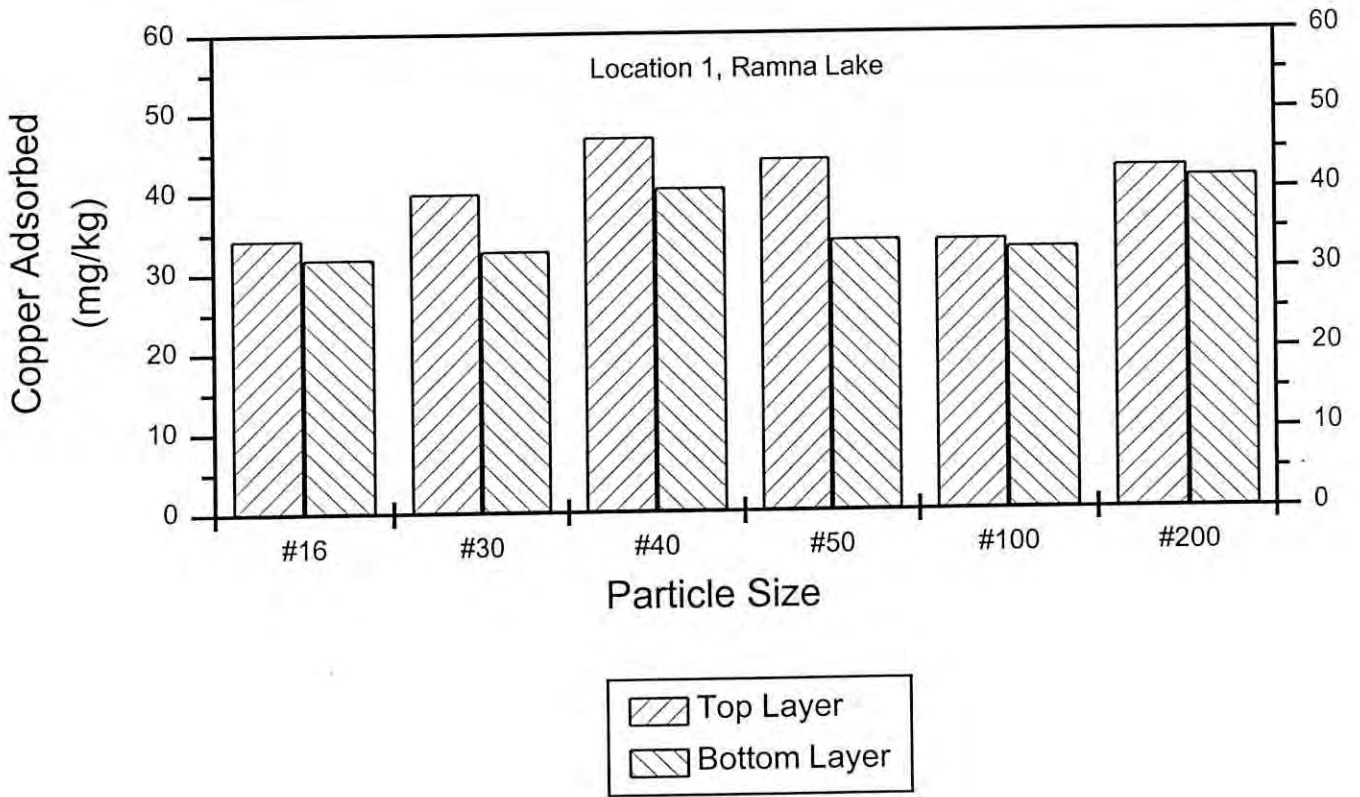


Fig. 4.44 : Copper Adsorption on Different Size of Particles

## *Conclusions*

1. In most cases the major portions of the sediment particles of both the lakes were retained on sieve #100 (0.149 mm) and sieve #200 (0.074 mm). Thus the major portion of particle ranged between 0.297 mm to 0.074 mm.
2. Particles retained on sieve #30, #40 and #50 (i.e. <1.19 mm to >0.297 mm) have major portion of copper adsorbed. However, particles retained on #40 (i.e. <0.59mm to >0.42mm) adsorbed maximum concentration of copper.
3. In Ramna lake maximum concentration of copper (weighted) was adsorbed on particle from Location 1 which may be attributed to the fact that it is the inlet point. In the Dhanmondi lake Location 2 represented maximum adsorbed copper which may also be attributed to the fact that it is located near the inlet points.
4. For both lakes it was found that locations receiving large waste loads contain high concentration of copper at the top layer. In the Dhanmondi lake Location 2 and in Ramna lake Location 1 receive high waste input. Weighted average of copper concentration at Location 1 of Ramna lake at the top sediment layer (38.57 mg/kg) was higher than bottom layer (34.39 mg/kg). Similarly at Location 2 of Dhanmondi lake copper concentration at top sediment layer (41.61 mg/kg) was higher than bottom sediment layer (38.67 mg/kg). It also indicates that these points have received more heavy metals in recent times than the previous years. From other points of these lakes it can be assessed that copper deposited in the sediment from time to time and accumulates on the deeper layer.
5. It was observed that in most of the cases copper adsorption increased with the decrease in particle size up to certain level (0.42mm). After that particle size copper adsorption decreased with the decrease in particle size.

6. Fineness Modulus (FM) and Uniformity Coefficient ( $C_u$ ) of Ramna lake was greater than Dhanmondi lake which indicates that overall grain size of Ramna lake is coarser than Dhanmondi lake.

#### 4.5 BIOACCUMULATION

Bioaccumulation of copper was studied by analyzing its accumulation in different parts of a fish. Thus a *Nilotica* fish was collected from Dhanmondi lake as it is the most common fish. A *Nilotica* is a bottom feeding collecting food from bottom sediment as well as overlying water. So it is most likely that copper accumulates on different tissues of *Nilotica* fish.

Concentration of copper (in mg/kg of wet mass) in various tissues such as gills, skin, muscle, stomach, external bones, head muscles are shown in Table 4.12 and are plotted in Fig 4.48. From these table and figure it is evident that maximum copper concentration is in stomach (7.442 mg/kg) among the various tissues of the fish. This may be attributed to the fact that the food (collected from the bottom sediment) digested by this fish is directly accumulated in the stomach. The next highest concentration of copper was present in gills (2.0302 mg/kg). Fish uses gills to intake water and use dissolved oxygen for respiration. Thus, copper in the water accumulates in the gills. Other tissues that are exposed are external bones i.e. fins (1.761 mg/kg) and skin (1.512 mg/kg) contain considerable amount of copper. Muscles and head muscle contain relatively less amount of copper (1.16 mg/l and 1.13 mg/l respectively). This indicates that heavy metals such as copper are present in excessive amount in the different parts of the fish in the Dhanmondi lake. Such fish, if consumed may be very harmful.

Table: 4.12 Copper concentration in different tissues of Nilotica Fish (mg/kg wet weight)

| Sl. No | Tissues of different parts of the fish | Concentration (mg/kg wet weight) |
|--------|--|----------------------------------|
| 1      | Gill                                   | 2.0302                           |
| 2      | Skin                                   | 1.5119                           |
| 3      | Muscle                                 | 1.1596                           |
| 4      | Stomach                                | 7.4419                           |
| 5      | External bone                          | 1.7613                           |
| 6      | Head Muscle                            | 1.1333                           |

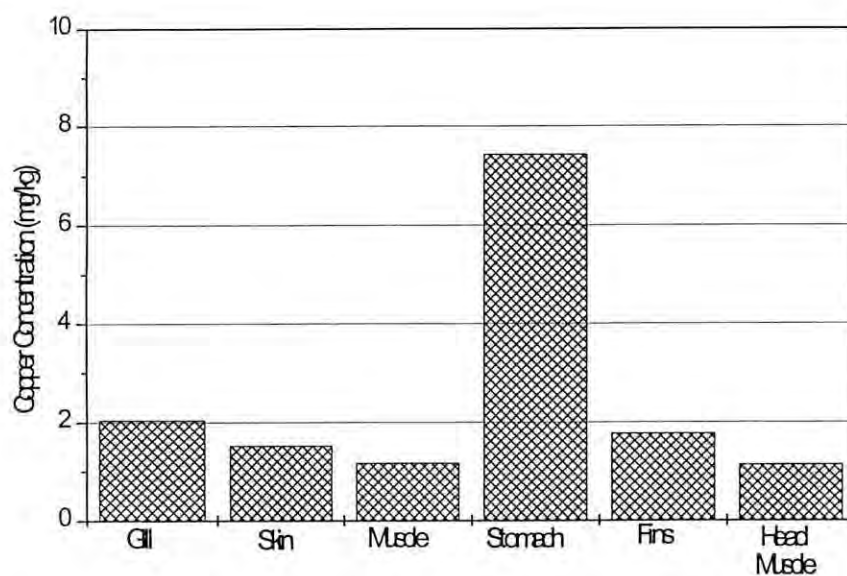


Figure: 4.45 Copper distribution at different tissues of Nilotica fish



## CHAPTER - 5

### CONCLUSION AND RECOMMENDATION

#### 5.1 CONCLUSIONS

The Dhanmondi lake and the Ramna lakes have been receiving considerable amount of domestic sewages for long period of time through the outfalls located at various points of the lakes. In addition surface run-off following rainfall contributes to the contamination of the water and sediment layer of these lakes. These point and non-point sources contain both metal as well as non-metallic pollutants. The primary objectives of the study was to assess the level of copper contamination in the lake water and sediment of Dhanmondi and Ramna lake. However other secondary objectives include assessment of toxic effects of the lake water by determining the equilibrium speciation of copper in Dhanmondi and Ramna lakes, spatial distribution of major copper species, copper adsorption characteristics depending on different sizes of bed particles and assessment of gross bioaccumulation of copper in fish.

Water and sediment samples of Dhanomndi and Ramna lake were collected from different sampling locations for laboratory analysis during three different period of the year namely, dry period (April to May), wet period (June-July) and intermediate period (August-January). Since major portion of copper get adsorbed on suspended sediment, then settle and accumulates on the bed, nature of copper adsorption depending on the bed particle characteristics was also studied. In addition, bioaccumulation of copper in fish species of the lake was assessed by determining copper concentration in gills and various tissues of a fish (*Nilotica*) of Dhanmondi lake.

Both the Dhanmondi and Ramna lake water and sediment layer indicate high level of copper contamination. However, contamination in Dhanmondi lake is much higher than that of Ramna lake.

Major copper species found in equilibrium analysis of the lake water columns of both the Dhanmondi and Ramna lakes were aqueous  $\text{Cu}(\text{OH})_2$ ,  $\text{Cu}^{2+}$ , aqueous  $\text{CuCO}_3$ . Concentration of aqueous  $\text{Cu}(\text{OH})_2$  was highest of all the Copper species.  $\text{Cu}^{2+}$ , the free form of copper species and more toxic of any other complex forms were also present in considerable amounts. pH was found to be the major controlling factor of copper speciation. With decrease in pH, ionic copper ( $\text{Cu}^{2+}$ ) concentration increases thus increasing the toxicity of water. Conversely, with the increase in pH, ionic copper concentration decreases with increased adsorption reducing toxicity.

Contribution of copper from bed sediment seem to play a significant role in equilibrium analysis. The major portion of particles of both the lakes were retained on sieve # 100 (0.149mm.) and sieve # 200 (0.074mm.). Thus, the particle size ranged between 0.297mm. to 0.074mm. However, adsorption of copper varied with size of particles. Maximum amount of copper was adsorbed on particles retained on sieve #30, #40, #50 (i.e. size < 1.19mm. to > 0.297mm.). In most cases copper absorption increased with the decrease in particle size upto a certain level (0.42 mm). After that particular particle size, copper absorption decreased with the decrease in particle size.

Study of bioaccumulation of copper revealed that heavy metals such as copper are present in excessive amount in the different parts of the fish in Dhanmondi lake. Maximum copper concentration was found in the stomach (7.442 mg/kg) among the various tissues of fish. Gills contained the next highest concentration of copper (2.03 mg/kg). Thus human consumption of the fishes from Dhanmondi lake may be harmful.

Study of copper adsorption on different sizes of bed sediments in Dhanmondi and Ramna lakes indicate that the deeper layer sediments are more contaminated with heavy metal such as copper. This is probably due to the accumulation of copper in the sediment following prolonged deposition of domestic as well as industrial sewage from these areas. At present, renovation work is underway at the Dhanmondi lake. It seems that the lake is being dredged indiscriminately and the dredged spoils are being piled along the shore. If not done upto a proper depth this dredging process is likely to expose the deeper sediment

layer which was found to be more contaminated with heavy metals. The overlying water, although fresh, will get contaminated with metals through diffusion and desorption from newly exposed bed. In addition, the dredged spoils piled up along the shore may release copper following rainfall into the lake and surrounding areas.

## 5.2 RECOMMENDATIONS

Continuous monitoring of the water and sediment layers of the Dhanmondi and Ramna lakes is essential to have a better view of situation. A temporal and seasonal variation study may be conducted in this regard. In addition, identification and estimation of pollutant loads to these lakes should be done. Effluents at all inlet points into the lake should be characterized along with their flow rates. Determination of temporal and spatial flow pattern should be done for modeling purpose.

Due to the technical difficulties analysis of organic contents could not be performed in this study. Inclusion of organic contents in the analysis will provide a more realistic and accurate results.

Particle setting velocities need to be assessed to determine the age of bed layer deposits. Copper level in lake may be assessed as a function of depth. These data will help in developing the history of copper contamination in Dhanmondi and Ramna lake. This will also help in predicting future copper levels in the lake bed sediment. In addition, current renovation work involving dredging operation may be properly performed with this information at hand.

Collection and analysis of deeper soil samples need to be done for better assessment of copper contamination on bed sediment. This will provide more information on biouptake mechanisms of organic biota.

Significant amount of copper has been found in fish tissues, it is necessary to assess long term effect of this contamination on pisciculture and also on people consuming fish from Dhanmondi lake.



## REFERENCES

Andrew, R.K., Biesinger, K.E., Glass, G.E., (1976); "Effect of inorganic complexing on the toxicity of copper to *Daphnia Magna*". Research vol. 11, pp 309 to 315, Pergamon Press 1977.

Badruzzaman, A.B.M., Lung, W.S. (1992); "Developing a modeling framework for metal speciation and transport in estuaries and coastal waters". Environmental Engineering Research Report No. 10, August 1992.

Batley, G.E., Gardner D. 1978, "A study of copper, lead and cadmium speciation in some estuarine and coastal marine science 7: 59-70.

Boyden; C.R., Aston, S.R. and Thorton, I. (1979), Tidal and seasonal variations of trace elements in two Cornish estuaries, "Estuarine and Coastal Marine Science", 9,303-317.

Burto, M.A.S. and Peterson, P.J. (1979), "Metal accumulation by aquatic bryophytes from polluted mine streams, Environmental Pollution", 19,39-46.

Chakoumakos, C and R.C. Russo and R.V. Thurston; "Toxicity of copper to Culthroat Trout (*Salmo clarki*) under differnt conditions of alkalinity, pH, Hardness", Environmental Science and Technology 13:213-219,1979.

De, A.K. (1994), Environmental Chemistry, Wiley Eastern Ltd. and New Age International Ltd., New Delhi.

Davles-Colley, R.J., Nelson, P.O., Williamson K.J. (1984); "Copper and Cadmium uptake by estuarine sedimentary phases".

Eisler, R. and Gardner. 1973; "Acute toxicology to an estuarine teleost of mixture of cadmium, copper and zinc salt". *Journal of fish biology* 5: 131-142.

Farley, K.J.; "Predicting organic accumulation in sediment near marine outfall", *Journal of Environmental Engineering*, Vol. 116, No.1, pp144-165,1990.

Gibbs, R.J. 1977; "Transport phases of transition metals in the Amazon and Yukon rivers". *Geological Society of America Bulletin*. 88: 829-843.

Hahney, H.C.H, and Kroontje, W. (1973), Significance of pH and chloride concentration on behavior of heavy metal pollution: mercury(II), cadmium(II), zinc(II) and lead(II), *Journal of Environmental Quality*, 2, 444-450.

Hansen, D.V., "Circulation, MESA, New York Bight Atlas Monograph-3", New York Sea Grant Institute, Albany, NY,1977.

Langmuir, D. (1980); "The mobility of Thorium in natural waters at low temperatures", *Geochimica et Cosmochimica Acta* Vol. 44, pp 1753 to 1766, Pergamon Press Ltd. 1980.

Lung, W.S., R.A. Rapaport, A.C. Franco, Predicting concentration of consumer product chemicals in estuaries, *Journal of Toxicology and Chemistry*, Vol. 9, No.9, pp 1127-1136, 1990.

Moore, J.W., Ramamoorthy, S. (1984); "Heavy metals in natural waters", Springer Verlag, New York.

Navo-Gradac, K.J., Wang P.F., (1984); "Water quality modeling in South San Francisco Bay". Draft of Speciation modeling of copper, ASCI corporation, US EPA ERL

Owens, M., Cornwell, J.C., 1995; "Sedimentary evidence for decreased heavy metal inputs to the Chesapeake Bay". *Ambio* Vol. 24, No.1, Feb. 1995.

Schecher, W.D. (1994), MINEQL+ : "A chemical equilibrium program for personal computer"; User's manual, Version 3.0

Stokes, P.M. 1975, "Adaptation of green algae to high levels of copper and nickel in aquatic environments". Int. T.C. Hutchinson (Ed.), *Proceedings of first international conference on heavy metals in the environment*. Vol. II University of Toronto Institute For Environmental Studies, Toronto, Canada. pp 137-154.

Tessier, A., Campbell, P.G.C., and Bisson, M. (1979), "Trace metal speciation in the Yamaska and St. Francois River (Quebec)". *Can. J., Earth Sci.*, Vol. 17, 1980.

Thomann, R.V., Mueller J.A., "Principles of surface water quality modelling and control". Harper and Row, New York.

Miller, T.G. and W.C. Mackay 1980. "The effect of hardness, alkalinity and pH of test water, on the toxicity of copper to rainbow trout." *Water Research* 14: 129-133.

Ramamoorthy, S. and Kushner, D.J. 1975; "Heavy metal binding components of river waters". *Journal of Fisheries Research Board of Canada* 32: 1755-1766.

Roth, I., and H. Hornung. 1977. "Heavy metal concentrations in water, sediments and fish from Mediterranean coastal area, Israel". *Environmental Science and Technology* 11: 265-269.

Trace metal speciation in the freshwater and estuarine regions of the Yarra River, Victoria Estuarine, *Coastal and Shelf Science*, 12, 353-374.

# **APPENDIX-A**



Table : Data for MINEQL<sup>+</sup> output for speciation of copper without considering contribution from sediment, Dhanmondi lake

|  | Location 1 |       |        | Location 2 |       |        | Location 3 |      |        | Location 4 |       |        | Location 5 |       |        | Location 6 |      |        | Location 7 |      |        |
|--|------------|-------|--------|------------|-------|--------|------------|------|--------|------------|-------|--------|------------|-------|--------|------------|------|--------|------------|------|--------|
|  | Dry        | Wet   | Inter. | Dry        | Wet   | Inter. | Dry        | Wet  | Inter. | Dry        | Wet   | Inter. | Dry        | Wet   | Inter. | Dry        | Wet  | Inter. | Dry        | Wet  | Inter. |
| Cu (aq.) (*10 <sup>-6</sup> ) (mol/l)                      | 3          | 2.4   | 2.4    | 3.1        | 2.3   | 3      | 2.9        | 1.7  | 2.2    | 3.1        | 1.8   | 2      | 3.3        | 1.8   | 1.5    | 3.3        | 2    | 2.1    | 3          | 1.6  | 2.4    |
| Cu (ss) (*10 <sup>-6</sup> ) (mol/l)                       | 2.4        | 0.9   | 0.5    | 1.5        | 1.1   | 0.3    | 1.1        | 0.9  | 0.8    | 0.5        | 1.1   | 0.4    | 0.6        | 1.4   | 0.5    | 0.3        | 1.2  | 0.2    | 1.7        | 1.7  | 10     |
| Cu (Total) (*10 <sup>-6</sup> ) (mol/l)                    | 5.4        | 3.3   | 2.9    | 4.6        | 3.5   | 3.4    | 4          | 2.6  | 3      | 3.6        | 2.9   | 2.4    | 3.9        | 3.2   | 2      | 3.6        | 3.2  | 2.3    | 4.9        | 3.4  | 3.5    |
| pH   | 7.66       | 7.8   | 7.8    | 7.8        | 7.4   | 7.2    | 7.7        | 7.5  | 7.3    | 7.7        | 7.4   | 8.7    | 7.88       | 8     | 8.1    | 7.8        | 7.6  | 7.3    | 7.94       | 7.9  | 8.3    |
| Temperature (°C)   | 31.3       | 31.3  | 20.5   | 31         | 31    | 19     | 31.2       | 30.3 | 19.5   | 30.9       | 29.5  | 20.5   | 31.6       | 30.5  | 1.5    | 31.2       | 30.5 | 20     | 31.3       | 30.5 | 20     |
| Alkalinity (*10 <sup>-3</sup> ) (mol/l)                    | 2.16       | 1.61  | 2.25   | 2.1        | 1.48  | 2.25   | 2.13       | 1.46 | 2.05   | 2.24       | 1.63  | 2.07   | 2.25       | 1.76  | 2.07   | 2.1        | 1.6  | 2.02   | 2.24       | 1.8  | 2.36   |
| Cl <sup>-1</sup> (*10 <sup>-3</sup> ) (mol/l)              | 3.19       | 1.31  | 1.5    | 2.9        | 1.42  | 1.55   | 2.91       | 1.34 | 1.64   | 2.68       | 1.23  | 1.78   | 2.37       | 1.24  | 1.64   | 3.2        | 1.4  | 1.69   | 3.85       | 3.12 | 4.06   |
| SO <sub>4</sub> <sup>-2</sup> (*10 <sup>-4</sup> ) (mol/l) | 4.5        | 3.75  | 4.8    | 4.26       | 4.7   | 6.3    | 4.4        | 6.25 | 7      | 7.65       | 6.25  | 6.4    | 6.3        | 5.3   | 6      | 5.26       | 7.2  | 7      | 5.7        | 1.2  | 4      |
| NO <sub>3</sub> <sup>-1</sup> (*10 <sup>-5</sup> ) (mol/l) | 3.27       | 3.27  | 3.27   | 3.27       | 3.27  | 3.27   | 3.27       | 3.27 | 3.27   | 3.27       | 3.27  | 3.27   | 3.27       | 3.27  | 3.27   | 3.27       | 3.27 | 3.27   | 3.27       | 3.27 | 3.27   |
| PO <sub>4</sub> <sup>-3</sup> (*10 <sup>-6</sup> ) (mol/l) | 4.21       | 4.21  | 4.21   | 4.21       | 4.21  | 4.21   | 4.21       | 4.21 | 4.21   | 4.21       | 4.21  | 4.21   | 4.21       | 4.21  | 4.21   | 4.21       | 4.21 | 4.21   | 4.21       | 4.21 | 4.21   |
| Na (*10 <sup>-4</sup> ) (mol/l)                            | 2.21       | 2.17  | 2.19   | 2.21       | 2.2   | 2.2    | 2.2        | 2.15 | 2.18   | 2.2        | 2.2   | 2.2    | 2.18       | 2.16  | 2.17   | 2.2        | 2.2  | 2.2    | 2.17       | 2.15 | 2.16   |
| K (*10 <sup>-4</sup> ) [(mol/l)]                           | 5.58       | 8.2   | 6.9    | 6.1        | 6.5   | 6.3    | 5.8        | 6.8  | 6.3    | 5.6        | 7.7   | 6.7    | 6.66       | 7.5   | 7.1    | 5          | 9.95 | 7.5    | 5.28       | 8.6  | 6.94   |
| Ca (*10 <sup>-3</sup> ) (mol/l)                            | 1.05       | 8.13  | 9.32   | 1.05       | 9.27  | 9.9    | 10         | 8.7  | 9.4    | 10.6       | 10    | 10.3   | 9.3        | 10.8  | 10.1   | 11.1       | 7.8  | 9.45   | 10         | 6.8  | 8.4    |
| Mg (*10 <sup>-4</sup> ) (mol/l)                            | 8.6        | 6.7   | 7.7    | 8.6        | 7.6   | 8.1    | 8.3        | 7.2  | 7.8    | 8.7        | 8.3   | 8.5    | 7.6        | 8.9   | 8.3    | 9.2        | 6.4  | 7.8    | 9.45       | 1    | 6.8    |
| % of total Cu on SS  | 44.4       | 27.27 | 17.24  | 32.6       | 31.43 | 8.82   | 27.5       | 34.6 | 26.67  | 13.89      | 37.93 | 16.67  | 15.39      | 43.75 | 25     | 8.3        | 37.5 | 8.7    | 34.7       | 50   | 28.6   |

Table : Data for MINEQL<sup>+</sup> output for speciation of copper without considering contribution from sediment, Ramna lake

|                                       | Location 1            |                       |                       | Location 2            |                       |                       | Location 3            |                       |                       | Location 4            |                       |                       |
|---------------------------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
|                                       | Dry                   | Wet                   | Interim               | Dry                   | Wet                   | Interim               | Dry                   | Wet                   | Interim               | Dry                   | Wet                   | Interim               |
| Cu (aq)(mol/l)                        | 2.9*10 <sup>-6</sup>  | 1.1*10 <sup>-6</sup>  | 1.83*10 <sup>-6</sup> | 2.94*10 <sup>-6</sup> | 2.6*10 <sup>-6</sup>  | 2.2*10 <sup>-6</sup>  | 2*10 <sup>-6</sup>    | 2*10 <sup>-6</sup>    | 1.6*10 <sup>-6</sup>  | 3.2*10 <sup>-6</sup>  | 1.7*10 <sup>-6</sup>  | 5.2*10 <sup>-6</sup>  |
| Cu (ss) (mol/l)                       | 0.6*10 <sup>-6</sup>  | 0.1*10 <sup>-6</sup>  | 1.3*10 <sup>-6</sup>  | 0.36*10 <sup>-6</sup> | 0.2*10 <sup>-6</sup>  | 0.5*10 <sup>-6</sup>  | 0.6*10 <sup>-6</sup>  | 0.4*10 <sup>-6</sup>  | 2.9*10 <sup>-6</sup>  | 0.2*10 <sup>-6</sup>  | 0.2*10 <sup>-6</sup>  | 0.4*10 <sup>-6</sup>  |
| Cu (Total)<br>(mol/l)                 | 3.5*10 <sup>-6</sup>  | 1.2*10 <sup>-6</sup>  | 3.2*10 <sup>-6</sup>  | 3.3*10 <sup>-6</sup>  | 2.8*10 <sup>-6</sup>  | 2.74*10 <sup>-6</sup> | 2.6*10 <sup>-6</sup>  | 2.4*10 <sup>-6</sup>  | 4.5*10 <sup>-6</sup>  | 3.4*10 <sup>-6</sup>  | 1.9*10 <sup>-6</sup>  | 5.6*10 <sup>-6</sup>  |
| pH                                    | 8.7                   | 7.3                   | 7.1                   | 8.9                   | 7.4                   | 7.5                   | 7.0                   | 8.0                   | 7.5                   | 8.9                   | 7.5                   | 7.4                   |
| Temperature<br>(°C)                   | 35                    | 33                    | 21                    | 34.5                  | 33.5                  | 20                    | 35                    | 33.5                  | 20                    | 34.5                  | 33                    | 20                    |
| Alkanity<br>(mol/l)                   | 1.56*10 <sup>-3</sup> | 1.51*10 <sup>-3</sup> | 1.8*10 <sup>-3</sup>  | 1.61*10 <sup>-3</sup> | 1.49*10 <sup>-3</sup> | 1.61*10 <sup>-3</sup> | 1.87*10 <sup>-3</sup> | 1.62*10 <sup>-3</sup> | 1.69*10 <sup>-3</sup> | 1.74*10 <sup>-3</sup> | 1.39*10 <sup>-3</sup> | 1.82*10 <sup>-3</sup> |
| Cl <sup>-1</sup> (mol/l)              | 1.35*10 <sup>-3</sup> | 0.65*10 <sup>-3</sup> | 1.2*10 <sup>-3</sup>  | 1*10 <sup>-3</sup>    | 0.71*10 <sup>-3</sup> | 0.96*10 <sup>-3</sup> | 1.07*10 <sup>-3</sup> | 0.67*10 <sup>-3</sup> | 0.85*10 <sup>-3</sup> | 1.04*10 <sup>-3</sup> | 0.9*10 <sup>-3</sup>  | 0.85*10 <sup>-3</sup> |
| SO <sub>4</sub> <sup>-2</sup> (mol/l) | 0.24*10 <sup>-3</sup> | 0.52*10 <sup>-3</sup> | 0.38*10 <sup>-3</sup> | 0.46*10 <sup>-3</sup> | 0.44*10 <sup>-3</sup> | 0.47*10 <sup>-3</sup> | 0.63*10 <sup>-3</sup> | 0.82*10 <sup>-3</sup> | 0.44*10 <sup>-3</sup> | 0.55*10 <sup>-3</sup> | 0.55*10 <sup>-3</sup> | 0.55*10 <sup>-3</sup> |
| NO <sub>3</sub> <sup>-1</sup> (mol/l) | 8*10 <sup>-6</sup>    | 8*10 <sup>-6</sup>    | 8*10 <sup>-6</sup>    | 8*10 <sup>-6</sup>    | 8*10 <sup>-6</sup>    | 8*10 <sup>-6</sup>    | 8*10 <sup>-6</sup>    | 8*10 <sup>-6</sup>    | 8*10 <sup>-6</sup>    | 8*10 <sup>-6</sup>    | 8*10 <sup>-6</sup>    | 8*10 <sup>-6</sup>    |
| PO <sub>4</sub> <sup>-3</sup> (mol/l) | 8*10 <sup>-6</sup>    | 8*10 <sup>-6</sup>    | 8*10 <sup>-6</sup>    | 8*10 <sup>-6</sup>    | 8*10 <sup>-6</sup>    | 8*10 <sup>-6</sup>    | 8*10 <sup>-6</sup>    | 8*10 <sup>-6</sup>    | 8*10 <sup>-6</sup>    | 8*10 <sup>-6</sup>    | 8*10 <sup>-6</sup>    | 8*10 <sup>-6</sup>    |
| Na (mol/l)                            | 2.19*10 <sup>-4</sup> | 2.19*10 <sup>-4</sup> | 2.19*10 <sup>-4</sup> | 2.19*10 <sup>-4</sup> | 2.19*10 <sup>-4</sup> | 2.19*10 <sup>-4</sup> | 2.19*10 <sup>-4</sup> | 2.19*10 <sup>-4</sup> | 2.19*10 <sup>-4</sup> | 2.19*10 <sup>-4</sup> | 2.19*10 <sup>-4</sup> | 2.19*10 <sup>-4</sup> |
| K (mol/l)                             | 6.81*10 <sup>-4</sup> | 6.81*10 <sup>-4</sup> | 6.81*10 <sup>-4</sup> | 6.81*10 <sup>-4</sup> | 6.81*10 <sup>-4</sup> | 6.81*10 <sup>-4</sup> | 6.81*10 <sup>-4</sup> | 6.81*10 <sup>-4</sup> | 6.81*10 <sup>-4</sup> | 6.81*10 <sup>-4</sup> | 6.81*10 <sup>-4</sup> | 6.81*10 <sup>-4</sup> |
| Ca (mol/l)                            | 9.54*10 <sup>-4</sup> | 9.54*10 <sup>-4</sup> | 9.54*10 <sup>-4</sup> | 9.54*10 <sup>-4</sup> | 9.54*10 <sup>-4</sup> | 9.54*10 <sup>-4</sup> | 9.54*10 <sup>-4</sup> | 9.54*10 <sup>-4</sup> | 9.54*10 <sup>-4</sup> | 9.54*10 <sup>-4</sup> | 9.54*10 <sup>-4</sup> | 9.54*10 <sup>-4</sup> |
| Mg (mol/l)                            | 7.86*10 <sup>-4</sup> | 7.86*10 <sup>-4</sup> | 7.86*10 <sup>-4</sup> | 7.86*10 <sup>-4</sup> | 7.86*10 <sup>-4</sup> | 7.86*10 <sup>-4</sup> | 7.86*10 <sup>-4</sup> | 7.86*10 <sup>-4</sup> | 7.86*10 <sup>-4</sup> | 7.86*10 <sup>-4</sup> | 7.86*10 <sup>-4</sup> | 7.86*10 <sup>-4</sup> |
| % of total Cu<br>on SS                | 17.14%                | 8.3%                  | 40.6%                 | 10.9%                 | 7.14%                 | 18.25%                | 23.07%                | 16.67%                | 64.45%                | 5.88%                 | 10.53%                | 7.14%                 |

Table : Data for MINEQL<sup>+</sup> output for speciation of copper with considering contribution from sediment, Dhanmondi lake

|  | Location 1 |      |        | Location 2 |      |        | Location 3 |      |        | Location 4 |      |        | Location 5 |      |        | Location 6 |      |        | Location 7 |      |        |
|--|------------|------|--------|------------|------|--------|------------|------|--------|------------|------|--------|------------|------|--------|------------|------|--------|------------|------|--------|
|  | Dry        | Wet  | Inter. | Dry        | Wet  | Inter. | Dry        | Wet  | Inter. | Dry        | Wet  | Inter. | Dry        | Wet  | Inter. | Dry        | Wet  | Inter. | Dry        | Wet  | Inter. |
| Cu (aq.) (*10 <sup>-6</sup> ) (mol/l)                      | 3          | 2.4  | 2.4    | 3.1        | 2.3  | 3      | 2.9        | 1.7  | 2.2    | 3.1        | 1.8  | 2      | 3.3        | 1.8  | 1.5    | 3.3        | 2    | 2.1    | 3          | 1.6  | 2.4    |
| Cu (ss) (*10 <sup>-5</sup> ) (mol/l)                       | 6.5        | 8.3  | 6.16   | 5.37       | 6.44 | 3.98   | 5.29       | 8.9  | 5.58   | 10.19      | 13.8 | 3.36   | 4.97       | 7.95 | 4.35   | 5.47       | 8.75 | 4.74   | 5.76       | 6.74 | 3.72   |
| Cu (Total) (*10 <sup>-5</sup> ) (mol/l)                    | 6.8        | 8.6  | 6.4    | 5.6        | 6.67 | 4.28   | 5.58       | 9.03 | 5.8    | 10.55      | 14   | 3.56   | 5.3        | 8.1  | 4.5    | 5.8        | 8.95 | 4.95   | 6.06       | 6.9  | 3.96   |
| pH   | 7.66       | 7.8  | 7.8    | 7.8        | 7.4  | 7.2    | 7.7        | 7.5  | 7.3    | 7.7        | 7.4  | 8.7    | 7.88       | 8    | 8.1    | 7.8        | 7.6  | 7.3    | 7.94       | 7.9  | 8.3    |
| Temperature (°C)   | 31.3       | 31.3 | 20.5   | 31         | 31   | 19     | 31.2       | 30.3 | 19.5   | 30.9       | 29.5 | 20.5   | 31.6       | 30.5 | 1.5    | 31.2       | 30.5 | 20     | 31.3       | 30.5 | 20     |
| Alkanity (*10 <sup>-3</sup> ) (mol/l)                      | 2.16       | 1.61 | 2.25   | 2.1        | 1.48 | 2.25   | 2.13       | 1.46 | 2.05   | 2.24       | 1.63 | 2.07   | 2.25       | 1.76 | 2.07   | 2.1        | 1.6  | 2.02   | 2.24       | 1.8  | 2.36   |
| Cl <sup>-1</sup> (*10 <sup>-3</sup> ) (mol/l)              | 3.19       | 1.31 | 1.5    | 2.9        | 1.42 | 1.55   | 2.91       | 1.34 | 1.64   | 2.68       | 1.23 | 1.78   | 2.37       | 1.24 | 1.64   | 3.2        | 1.4  | 1.69   | 3.85       | 3.12 | 4.06   |
| SO <sub>4</sub> <sup>-2</sup> (*10 <sup>-4</sup> ) (mol/l) | 4.5        | 3.75 | 4.8    | 4.26       | 4.7  | 6.3    | 4.4        | 6.25 | 7      | 7.65       | 6.25 | 6.4    | 6.3        | 5.3  | 6      | 5.26       | 7.2  | 7      | 5.7        | 1.2  | 4      |
| NO <sub>3</sub> <sup>-1</sup> (*10 <sup>-5</sup> ) (mol/l) | 3.27       | 3.27 | 3.27   | 3.27       | 3.27 | 3.27   | 3.27       | 3.27 | 3.27   | 3.27       | 3.27 | 3.27   | 3.27       | 3.27 | 3.27   | 3.27       | 3.27 | 3.27   | 3.27       | 3.27 | 3.27   |
| PO <sub>4</sub> <sup>-3</sup> (*10 <sup>-6</sup> ) (mol/l) | 4.21       | 4.21 | 4.21   | 4.21       | 4.21 | 4.21   | 4.21       | 4.21 | 4.21   | 4.21       | 4.21 | 4.21   | 4.21       | 4.21 | 4.21   | 4.21       | 4.21 | 4.21   | 4.21       | 4.21 | 4.21   |
| Na (*10 <sup>-4</sup> ) (mol/l)                            | 2.21       | 2.17 | 2.19   | 2.21       | 2.2  | 2.2    | 2.2        | 2.15 | 2.18   | 2.2        | 2.2  | 2.2    | 2.18       | 2.16 | 2.17   | 2.2        | 2.2  | 2.2    | 2.17       | 2.15 | 2.16   |
| K (*10 <sup>-4</sup> ) [(mol/l)]                           | 5.58       | 8.2  | 6.9    | 6.1        | 6.5  | 6.3    | 5.8        | 6.8  | 6.3    | 5.6        | 7.7  | 6.7    | 6.66       | 7.5  | 7.1    | 5          | 9.95 | 7.5    | 5.28       | 8.6  | 6.94   |
| Ca (*10 <sup>-3</sup> ) (mol/l)                            | 1.05       | 8.13 | 9.32   | 1.05       | 9.27 | 9.9    | 10         | 8.7  | 9.4    | 10.6       | 10   | 10.3   | 9.3        | 10.8 | 10.1   | 11.1       | 7.8  | 9.45   | 10         | 6.8  | 8.4    |
| Mg (*10 <sup>-4</sup> ) (mol/l)                            | 8.6        | 6.7  | 7.7    | 8.6        | 7.6  | 8.1    | 8.3        | 7.2  | 7.8    | 8.7        | 8.3  | 8.5    | 7.6        | 8.9  | 8.3    | 9.2        | 6.4  | 7.8    | 9.45       | 1    | 6.8    |
| % of total Cu on SS  | 95.6       | 77.2 | 96     | 95.89      | 96.6 | 92.99  | 94.8       | 98.1 | 96.2   | 96.6       | 98.7 | 94.4   | 93.8       | 98.1 | 96.6   | 94.3       | 97.8 | 95.8   | 95.05      | 97.7 | 93.94  |

Table : Data for MINEQL<sup>+</sup> output for speciation of copper with considering contribution from sediment, Ramna lake

|                                       | Location 1            |                       |                       | Location 2            |                       |                       | Location 3            |                       |                       | Location 4            |                       |                       |
|---------------------------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
|                                       | Dry                   | Wet                   | Interim               | Dry                   | Wet                   | Interim               | Dry                   | Wet                   | Interim               | Dry                   | Wet                   | Interim               |
| Cu (aq)(mol/l)                        | 2.9*10 <sup>-6</sup>  | 1.1*10 <sup>-6</sup>  | 1.83*10 <sup>-6</sup> | 2.94*10 <sup>-6</sup> | 2.6*10 <sup>-6</sup>  | 2.2*10 <sup>-6</sup>  | 2*10 <sup>-6</sup>    | 2*10 <sup>-6</sup>    | 1.6*10 <sup>-6</sup>  | 3.2*10 <sup>-6</sup>  | 1.7*10 <sup>-6</sup>  | 5.2*10 <sup>-6</sup>  |
| Cu (ss) (mol/l)                       | 6.11*10 <sup>-5</sup> | 7.4*10 <sup>-5</sup>  | 5.82*10 <sup>-5</sup> | 5.88*10 <sup>-5</sup> | 6.6*10 <sup>-5</sup>  | 4.8*10 <sup>-5</sup>  | 5.68*10 <sup>-5</sup> | 6.1*10 <sup>-5</sup>  | 5.1*10 <sup>-5</sup>  | 7.09*10 <sup>-5</sup> | 8.37*10 <sup>-5</sup> | 5.6*10 <sup>-5</sup>  |
| Cu (Total)<br>(mol/l)                 | 6.4*10 <sup>-5</sup>  | 7.6*10 <sup>-5</sup>  | 6.04*10 <sup>-5</sup> | 6.2*10 <sup>-5</sup>  | 6.9*10 <sup>-5</sup>  | 5*10 <sup>-5</sup>    | 5.88*10 <sup>-5</sup> | 6.3*10 <sup>-5</sup>  | 5.26*10 <sup>-5</sup> | 7.4*10 <sup>-5</sup>  | 8.56*10 <sup>-5</sup> | 6.1*10 <sup>-5</sup>  |
| pH                                    | 8.7                   | 7.3                   | 7.1                   | 8.9                   | 7.4                   | 7.5                   | 7.0                   | 8.0                   | 7.5                   | 8.9                   | 7.5                   | 7.4                   |
| Temperature<br>(°C)                   | 35                    | 33                    | 21                    | 34.5                  | 33.5                  | 20                    | 35                    | 33.5                  | 20                    | 34.5                  | 33                    | 20                    |
| Alkanity<br>(mol/l)                   | 1.56*10 <sup>-3</sup> | 1.51*10 <sup>-3</sup> | 1.8*10 <sup>-3</sup>  | 1.61*10 <sup>-3</sup> | 1.49*10 <sup>-3</sup> | 1.61*10 <sup>-3</sup> | 1.87*10 <sup>-3</sup> | 1.62*10 <sup>-3</sup> | 1.69*10 <sup>-3</sup> | 1.74*10 <sup>-3</sup> | 1.39*10 <sup>-3</sup> | 1.82*10 <sup>-3</sup> |
| Cl <sup>-1</sup> (mol/l)              | 1.35*10 <sup>-3</sup> | 0.65*10 <sup>-3</sup> | 1.2*10 <sup>-3</sup>  | 1*10 <sup>-3</sup>    | 0.71*10 <sup>-3</sup> | 0.96*10 <sup>-3</sup> | 1.07*10 <sup>-3</sup> | 0.67*10 <sup>-3</sup> | 0.85*10 <sup>-3</sup> | 1.04*10 <sup>-3</sup> | 0.9*10 <sup>-3</sup>  | 0.85*10 <sup>-3</sup> |
| SO <sub>4</sub> <sup>-2</sup> (mol/l) | 0.24*10 <sup>-3</sup> | 0.52*10 <sup>-3</sup> | 0.38*10 <sup>-3</sup> | 0.46*10 <sup>-3</sup> | 0.44*10 <sup>-3</sup> | 0.47*10 <sup>-3</sup> | 0.63*10 <sup>-3</sup> | 0.82*10 <sup>-3</sup> | 0.44*10 <sup>-3</sup> | 0.55*10 <sup>-3</sup> | 0.55*10 <sup>-3</sup> | 0.55*10 <sup>-3</sup> |
| NO <sub>3</sub> <sup>-1</sup> (mol/l) | 8*10 <sup>-6</sup>    | 8*10 <sup>-6</sup>    | 8*10 <sup>-6</sup>    | 8*10 <sup>-6</sup>    | 8*10 <sup>-6</sup>    | 8*10 <sup>-6</sup>    | 8*10 <sup>-6</sup>    | 8*10 <sup>-6</sup>    | 8*10 <sup>-6</sup>    | 8*10 <sup>-6</sup>    | 8*10 <sup>-6</sup>    | 8*10 <sup>-6</sup>    |
| PO <sub>4</sub> <sup>-3</sup> (mol/l) | 8*10 <sup>-6</sup>    | 8*10 <sup>-6</sup>    | 8*10 <sup>-6</sup>    | 8*10 <sup>-6</sup>    | 8*10 <sup>-6</sup>    | 8*10 <sup>-6</sup>    | 8*10 <sup>-6</sup>    | 8*10 <sup>-6</sup>    | 8*10 <sup>-6</sup>    | 8*10 <sup>-6</sup>    | 8*10 <sup>-6</sup>    | 8*10 <sup>-6</sup>    |
| Na (mol/l)                            | 2.19*10 <sup>-4</sup> | 2.19*10 <sup>-4</sup> | 2.19*10 <sup>-4</sup> | 2.19*10 <sup>-4</sup> | 2.19*10 <sup>-4</sup> | 2.19*10 <sup>-4</sup> | 2.19*10 <sup>-4</sup> | 2.19*10 <sup>-4</sup> | 2.19*10 <sup>-4</sup> | 2.19*10 <sup>-4</sup> | 2.19*10 <sup>-4</sup> | 2.19*10 <sup>-4</sup> |
| K (mol/l)                             | 6.81*10 <sup>-4</sup> | 6.81*10 <sup>-4</sup> | 6.81*10 <sup>-4</sup> | 6.81*10 <sup>-4</sup> | 6.81*10 <sup>-4</sup> | 6.81*10 <sup>-4</sup> | 6.81*10 <sup>-4</sup> | 6.81*10 <sup>-4</sup> | 6.81*10 <sup>-4</sup> | 6.81*10 <sup>-4</sup> | 6.81*10 <sup>-4</sup> | 6.81*10 <sup>-4</sup> |
| Ca (mol/l)                            | 9.54*10 <sup>-4</sup> | 9.54*10 <sup>-4</sup> | 9.54*10 <sup>-4</sup> | 9.54*10 <sup>-4</sup> | 9.54*10 <sup>-4</sup> | 9.54*10 <sup>-4</sup> | 9.54*10 <sup>-4</sup> | 9.54*10 <sup>-4</sup> | 9.54*10 <sup>-4</sup> | 9.54*10 <sup>-4</sup> | 9.54*10 <sup>-4</sup> | 9.54*10 <sup>-4</sup> |
| Mg (mol/l)                            | 7.86*10 <sup>-4</sup> | 7.86*10 <sup>-4</sup> | 7.86*10 <sup>-4</sup> | 7.86*10 <sup>-4</sup> | 7.86*10 <sup>-4</sup> | 7.86*10 <sup>-4</sup> | 7.86*10 <sup>-4</sup> | 7.86*10 <sup>-4</sup> | 7.86*10 <sup>-4</sup> | 7.86*10 <sup>-4</sup> | 7.86*10 <sup>-4</sup> | 7.86*10 <sup>-4</sup> |
| % of total Cu<br>on SS                | 95.5                  | 98.6                  | 96.3                  | 94.77                 | 96.2                  | 95.6                  | 96.6                  | 96.8                  | 96.97                 | 95.8                  | 98.1                  | 91.3                  |



## **APPENDIX-B**

MINEQL output for speciation of copper without considering contribution from sediment

Location 1(Dry Period),Dhanmondi Lake

| Name  | Conc.       | %Total |
|---|-------------|--------|
| Cu(2+)  | 7.42E-08    | 1.4    |
| Cu <sub>2</sub> (OH) <sub>2</sub> +2 (+2)           | 4.24E-10    | 0      |
| Cu(OH) <sub>3</sub> - (-1)                          | 8.94E-12    | 0      |
| Cu(OH) <sub>4</sub> -2 (-2)                         | 1.15E-16    | 0      |
| CuOH + (+1)   | 2.86E-08    | 0      |
| Cu(OH) <sub>2</sub> AQ                              | 0.00000273  | 50.5   |
| CuHCO <sub>3</sub> + (+1)                           | 6.25E-09    | 0      |
| CuHPO <sub>4</sub>                                  | 4.05E-11    | 0      |
| Fe(st)OCu (+1)                                      | 0.000000133 | 2.5    |
| *Fe(wk)OCu (+1)                                     | 0.00000227  | 42.1   |
| CuCl <sub>3</sub> - (-1)                            | 7.45E-18    | 0      |
| CuCl <sub>2</sub> AQ                                | 6.56E-13    | 0      |
| CuCl <sub>4</sub> -2 1 (-2)                         | 1.42E-22    | 0      |
| CuCl + (+1)   | 4.53E-10    | 0      |
| CuCO <sub>3</sub> AQ                                | 0.000000153 | 2.8    |
| Cu(CO <sub>3</sub> ) <sub>2</sub> -2 (-2)           | 1.48E-10    | 0      |
| CuSO <sub>4</sub> AQ                                | 2.92E-09    | 0      |
| ATACAMITE   | 0.0459      | *****  |
| AZURITE   | 0.00886     | *****  |
| MALACHITE   | 0.564       | *****  |
| TENORITE  | 3.13        | *****  |
| CU(OH) <sub>2</sub>                                 | 0.299       | *****  |
| CUPRICFERIT   | 0.0169      | *****  |
| CU <sub>2</sub> (OH) <sub>3</sub> NO <sub>3</sub>   | 0.00000596  | *****  |
| ANTLERITE   | 0.00125     | *****  |
| CUOCUSO <sub>4</sub>                                | 5.5E-15     | *****  |
| BROCHANTITE   | 0.0145      | *****  |
| LANGITE   | 0.000516    | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ,3W | 1.78E-11    | *****  |
| CHALCANTHITE  | 6.24E-09    | *****  |
| MELANOTHALLI  | 8.45E-17    | *****  |
| CUCO <sub>3</sub>                                   | 0.000122    | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>     | 9.54E-10    | *****  |
| CUSO <sub>4</sub>                                   | 1.4E-14     | *****  |

MINEQL output for speciation of copper without considering contribution from sediment

Location 1 (Wet Period), Dhanmondi Lake

| Name            | Conc.       | %Total |
|-----------------|-------------|--------|
| Cu(2+)          | 3.12E-08    | 0      |
| Cu2(OH)2+2 (+2) | 2.68E-10    | 0      |
| Cu(OH)3 - (-1)  | 9.88E-12    | 0      |
| Cu(OH)4 -2 (-2) | 1.68E-16    | 0      |
| CuOH + (+1)     | 1.69E-08    | 0      |
| Cu(OH)2 AQ      | 0.00000223  | 67.4   |
| CuHCO3 + (+1)   | 3.76E-09    | 0      |
| CuHPO4          | 1.15E-11    | 0      |
| Fe(st)OCu (+1)  | 5.76E-08    | 1.7    |
| *Fe(wk)OCu (+1) | 0.000000835 | 25.3   |
| CuCl3 - (-1)    | 3.67E-19    | 0      |
| CuCl2 AQ        | 7.08E-14    | 0      |
| CuCl4 -2 1 (-2) | 2.28E-24    | 0      |
| CuCl + (+1)     | 1.1E-10     | 0      |
| CuCO3 AQ        | 0.000000128 | 3.9    |
| Cu(CO3)2-2 (-2) | 2.25E-10    | 0      |
| CuSO4 AQ        | 1.17E-09    | 0      |
| ATACAMITE       | 0.0178      | *****  |
| AZURITE         | 0.0115      | *****  |
| MALACHITE       | 0.66        | *****  |
| TENORITE        | 4.35        | *****  |
| CU(OH)2         | 0.416       | *****  |
| CUPRICFERIT     | 0.0181      | *****  |
| CU2(OH)3NO3     | 0.00000533  | *****  |
| ANTLERITE       | 0.000318    | *****  |
| CUOCUSO4        | 5.96E-15    | *****  |
| BROCHANTITE     | 0.00302     | *****  |
| LANGITE         | 0.000428    | *****  |
| CU3(PO4)2,3W    | 1.17E-12    | *****  |
| CHALCANTHITE    | 2.27E-09    | *****  |
| MELANOTHALLI    | 9.7E-18     | *****  |
| CUCO3           | 0.000101    | *****  |
| CU3(PO4)2       | 6.28E-11    | *****  |
| CUSO4           | 1.01E-14    | *****  |

MINEQL output for speciation of copper without considering contribution from sediment

Location 1 (Intermediate Period), Dhanmondi Lake

| Name  | Conc.       | %Total |
|---|-------------|--------|
| Cu(2+)  | 3.14E-08    | 1.1    |
| Cu <sub>2</sub> (OH) <sub>2</sub> +2 (+2)           | 9.29E-11    | 0      |
| Cu(OH) <sub>3</sub> - (-1)                          | 9.94E-12    | 0      |
| Cu(OH) <sub>4</sub> -2 (-2)                         | 1.71E-16    | 0      |
| CuOH + (+1)   | 1.69E-08    | 0      |
| Cu(OH) <sub>2</sub> AQ                              | 0.00000223  | 76.8   |
| CuHCO <sub>3</sub> + (+1)                           | 3.64E-09    | 0      |
| CuHPO <sub>4</sub>                                  | 1.56E-11    | 0      |
| Fe(st)OCu (+1)                                      | 3.05E-08    | 1.1    |
| *Fe(wk)OCu (+1)                                     | 0.000000466 | 16.1   |
| CuCl <sub>3</sub> - (-1)                            | 2.37E-19    | 0      |
| CuCl <sub>2</sub> AQ                                | 4.83E-14    | 0      |
| CuCl <sub>4</sub> -2 1 (-2)                         | 2.43E-24    | 0      |
| CuCl + (+1)   | 7.38E-11    | 0      |
| CuCO <sub>3</sub> AQ                                | 0.000000123 | 4.3    |
| Cu(CO <sub>3</sub> ) <sub>2</sub> -2 (-2)           | 2.15E-10    | 0      |
| CuSO <sub>4</sub> AQ                                | 1.38E-09    | 0      |
| ATACAMITE   | 0.0065      | *****  |
| AZURITE   | 0.00253     | *****  |
| MALACHITE   | 0.248       | *****  |
| TENORITE  | 1.72        | *****  |
| CU(OH) <sub>2</sub>                                 | 0.165       | *****  |
| CUPRICFERIT   | 0.0113      | *****  |
| CU <sub>2</sub> (OH) <sub>3</sub> NO <sub>3</sub>   | 0.00000185  | *****  |
| ANTLERITE   | 0.0004      | *****  |
| CUOCUSO <sub>4</sub>                                | 8.61E-16    | *****  |
| BROCHANTITE   | 0.0038      | *****  |
| LANGITE   | 0.0000484   | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ,3W | 2.16E-12    | *****  |
| CHALCANTHITE  | 3.11E-09    | *****  |
| MELANOTHALLI  | 5.94E-18    | *****  |
| CUCO <sub>3</sub>                                   | 0.0000981   | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>     | 1.16E-10    | *****  |
| CUSO <sub>4</sub>                                   | 4.2E-15     | *****  |



MINEQL output for speciation of copper without considering contribution from sediment

Location 2 (Dry Period), Dhanmondi Lake

| Name  | Conc.       | %Total |
|---|-------------|--------|
| Cu(2+)  | 4.08E-08    | 0      |
| Cu <sub>2</sub> (OH) <sub>2</sub> +2 (+2)           | 4.37E-10    | 0      |
| Cu(OH) <sub>3</sub> - (-1)                          | 1.29E-11    | 0      |
| Cu(OH) <sub>4</sub> -2 (-2)                         | 2.3E-16     | 0      |
| CuOH + (+1)   | 2.17E-08    | 0      |
| Cu(OH) <sub>2</sub> AQ                              | 0.00000285  | 62.1   |
| CuHCO <sub>3</sub> + (+1)                           | 4.82E-09    | 0      |
| CuHPO <sub>4</sub>                                  | 1.01E-11    | 0      |
| Fe(st)OCu (+1)                                      | 9.36E-08    | 2      |
| *Fe(wk)OCu (+1)                                     | 0.00000142  | 30.8   |
| CuCl <sub>3</sub> - (-1)                            | 4.79E-18    | 0      |
| CuCl <sub>2</sub> AQ                                | 4.19E-13    | 0      |
| CuCl <sub>4</sub> -2 1 (-2)                         | 6.8E-23     | 0      |
| CuCl + (+1)   | 3E-10       | 0      |
| CuCO <sub>3</sub> AQ                                | 0.000000163 | 3.6    |
| Cu(CO <sub>3</sub> ) <sub>2</sub> -2 (-2)           | 3.07E-10    | 0      |
| CuSO <sub>4</sub> AQ                                | 1.56E-09    | 0      |
| ATACAMITE   | 0.0614      | *****  |
| AZURITE   | 0.0232      | *****  |
| MALACHITE   | 1.06        | *****  |
| TENORITE  | 5.44        | *****  |
| CU(OH) <sub>2</sub>                                 | 0.52        | *****  |
| CUPRICFERIT   | 0.023       | *****  |
| CU <sub>2</sub> (OH) <sub>3</sub> NO <sub>3</sub>   | 0.00000834  | *****  |
| ANTLERITE   | 0.0007      | *****  |
| CUOCUSO <sub>4</sub>                                | 9.64E-15    | *****  |
| BROCHANTITE   | 0.00853     | *****  |
| LANGITE   | 0.00113     | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ,3W | 1.15E-12    | *****  |
| CHALCANTHITE  | 3.04E-09    | *****  |
| MELANOTHALLI  | 5.73E-17    | *****  |
| CUCO <sub>3</sub>                                   | 0.00013     | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>     | 6.2E-11     | *****  |
| CUSO <sub>4</sub>                                   | 1.31E-14    | *****  |

MINEQL out put for speciation of copper without considering contribution from sediment

Location 2(Wet Period),Dhanmondi Lake

| Name            | Conc.       | %Total |
|-----------------|-------------|--------|
| Cu(2+)          | 0.000000181 | 5.2    |
| Cu2(OH)2+2 (+2) | 1.39E-09    | 0      |
| Cu(OH)3 - (-1)  | 3.63E-12    | 0      |
| Cu(OH)4 -2 (-2) | 2.49E-17    | 0      |
| CuOH + (+1)     | 3.89E-08    | 1.1    |
| Cu(OH)2 AQ      | 0.00000204  | 58.3   |
| CuHCO3 + (+1)   | 8.66E-09    | 0      |
| CuHPO4          | 1.88E-10    | 0      |
| Fe(st)OCu (+1)  | 5.55E-08    | 1.6    |
| *Fe(wk)OCu (+1) | 0.00000105  | 29.9   |
| CuCl3 - (-1)    | 2.62E-18    | 0      |
| CuCl2 AQ        | 4.68E-13    | 0      |
| CuCl -2 1 (-2)  | 1.79E-23    | 0      |
| CuCl + (+1)     | 6.74E-10    | 0      |
| CuCO3 AQ        | 0.000000117 | 3.3    |
| Cu(CO3)2-2 (-2) | 3.32E-11    | 0      |
| CuSO4 AQ        | 8.19E-09    | 0      |
| ATACAMITE       | 0.0393      | *****  |
| AZURITE         | 0.00849     | *****  |
| MALACHITE       | 0.541       | *****  |
| TENORITE        | 3.89        | *****  |
| CU(OH)2         | 0.372       | *****  |
| CUPRICFERIT     | 0.0164      | *****  |
| CU2(OH)3NO3     | 0.0000109   | *****  |
| ANTLERITE       | 0.00189     | *****  |
| CUOCUSO4        | 3.63E-14    | *****  |
| BROCHANTITE     | 0.0164      | *****  |
| LANGITE         | 0.00218     | *****  |
| CU3(PO4)2,3W    | 2.86E-10    | *****  |
| CHALCANTHITE    | 0.000000016 | *****  |
| MELANOTHALLI    | 6.39E-17    | *****  |
| CUCO3           | 0.0000928   | *****  |
| CU3(PO4)2       | 1.54E-08    | *****  |
| CUSO4           | 6.88E-14    | *****  |

MINEQL output for speciation of copper without considering contribution from sediment

Location 3(Intermediate Period), Dhanmondi Lake

| Name  | Conc.       | %Total |
|---|-------------|--------|
| Cu(2+)  | 0.000000526 | 15.5   |
| Cu <sub>2</sub> (OH) <sub>2</sub> +2 (+2)           | 1.39E-09    | 0      |
| Cu(OH) <sub>3</sub> - (-1)                          | 2.64E-12    | 0      |
| Cu(OH) <sub>4</sub> -2 (-2)                         | 1.17E-17    | 0      |
| CuOH + (+1)   | 7.02E-08    | 2.1    |
| Cu(OH) <sub>2</sub> AQ                              | 0.00000233  | 68.4   |
| CuHCO <sub>3</sub> + (+1)                           | 1.51E-08    | 0      |
| CuHPO <sub>4</sub>                                  | 7.83E-11    | 0      |
| Fe(st)OCu (+1)                                      | 3.72E-09    | 0      |
| *Fe(wk)OCu (+1)                                     | 0.000000301 | 8.8    |
| CuCl <sub>3</sub> - (-1)                            | 3.73E-18    | 0      |
| CuCl <sub>2</sub> AQ                                | 7.57E-13    | 0      |
| CuCl <sub>4</sub> -2 1 (-2)                         | 4.22E-23    | 0      |
| CuCl + (+1)   | 1.15E-09    | 0      |
| CuCO <sub>3</sub> AQ                                | 0.000000128 | 3.8    |
| Cu(CO <sub>3</sub> ) <sub>2</sub> -2 (-2)           | 1.46E-11    | 0      |
| CuSO <sub>4</sub> AQ                                | 2.71E-08    | 0      |
| ATACAMITE   | 0.0244      | *****  |
| AZURITE   | 0.00232     | *****  |
| MALACHITE   | 0.234       | *****  |
| TENORITE  | 1.57        | *****  |
| CU(OH) <sub>2</sub>                                 | 0.15        | *****  |
| CUPRICFERIT   | 0.011       | *****  |
| CU <sub>2</sub> (OH) <sub>3</sub> NO <sub>3</sub>   | 0.00000679  | *****  |
| ANTLERITE   | 0.00878     | *****  |
| CUOCUSO <sub>4</sub>                                | 1.32E-14    | *****  |
| BROCHANTITE   | 0.0871      | *****  |
| LANGITE   | 0.000783    | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ,3W | 5.68E-11    | *****  |
| CHALCANTHITE  | 6.34E-08    | *****  |
| MELANOTHALLI  | 9.17E-17    | *****  |
| CUCO <sub>3</sub>                                   | 0.000102    | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>     | 3.05E-09    | *****  |
| CUSO <sub>4</sub>                                   | 7.2E-14     | *****  |

MINEQL output for speciation of copper without considering contribution from sediment

Location 3 (Dry Period), Dhanmondi Lake

| Name  | Conc.       | %Total |
|---|-------------|--------|
| Cu(2+)  | 5.84E-08    | 1.5    |
| Cu <sub>2</sub> (OH) <sub>2</sub> +2 (+2)           | 5.93E-10    | 0      |
| Cu(OH) <sub>3</sub> - (-1)                          | 9.28E-12    | 0      |
| Cu(OH) <sub>4</sub> -2 (-2)                         | 1.24E-16    | 0      |
| CuOH + (+1)   | 2.53E-08    | 0      |
| Cu(OH) <sub>2</sub> AQ                              | 0.00000265  | 66.3   |
| CuHCO <sub>3</sub> + (+1)                           | 5.64E-09    | 0      |
| CuHPO <sub>4</sub>                                  | 1.47E-09    | 0      |
| Fe(st)OCu (+1)                                      | 4.98E-08    | 1.2    |
| *Fe(wk)OCu (+1)                                     | 0.00000105  | 26.3   |
| CuCl <sub>3</sub> - (-1)                            | 7.64E-18    | 0      |
| CuCl <sub>2</sub> AQ                                | 6.64E-13    | 0      |
| CuCl <sub>4</sub> -2 1 (-2)                         | 1.05E-22    | 0      |
| CuCl + (+1)   | 4.6E-10     | 0      |
| CuCO <sub>3</sub> AQ                                | 0.000000152 | 3.8    |
| Cu(CO <sub>3</sub> ) <sub>2</sub> -2 (-2)           | 1.66E-10    | 0      |
| CuSO <sub>4</sub> AQ                                | 2.81E-09    | 0      |
| ATACAMITE   | 0.0702      | *****  |
| AZURITE   | 0.0191      | *****  |
| MALACHITE   | 0.928       | *****  |
| TENORITE  | 5.14        | *****  |
| CU(OH) <sub>2</sub>                                 | 0.491       | *****  |
| CUPRICFERIT   | 0.0215      | *****  |
| CU <sub>2</sub> (OH) <sub>3</sub> NO <sub>3</sub>   | 0.00000948  | *****  |
| ANTLERITE   | 0.00109     | *****  |
| CUOCUSO <sub>4</sub>                                | 1.68E-14    | *****  |
| BROCHANTITE   | 0.0123      | *****  |
| LANGITE   | 0.00171     | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ,3W | 2.28E-08    | *****  |
| CHALCANTHITE  | 5.49E-09    | *****  |
| MELANOTHALLI  | 9.09E-17    | *****  |
| CUCO <sub>3</sub>                                   | 0.000121    | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>     | 0.00000122  | *****  |
| CUSO <sub>4</sub>                                   | 2.41E-14    | *****  |



MINEQL output for speciation of copper without considering contribution from sediment

Location 3 (wet Period), Dhanmondi Lake

| Name  | Conc.       | %Total |
|---|-------------|--------|
| Cu(2+)  | 8.41E-08    | 3.2    |
| Cu <sub>2</sub> (OH) <sub>2</sub> +2 (+2)           | 4.43E-10    | 0      |
| Cu(OH) <sub>3</sub> - (-1)                          | 3.36E-12    | 0      |
| Cu(OH) <sub>4</sub> -2 (-2)                         | 2.9E-17     | 0      |
| CuOH + (+1)   | 2.27E-08    | 0      |
| Cu(OH) <sub>2</sub> AQ                              | 0.0000015   | 57.7   |
| CuHCO <sub>3</sub> + (+1)                           | 5.04E-09    | 0      |
| CuHPO <sub>4</sub>                                  | 7.55E-11    | 0      |
| Fe(st)OCu (+1)                                      | 5.03E-08    | 1.9    |
| *Fe(wk)OCu (+1)                                     | 0.000000346 | 32.5   |
| CuCl <sub>3</sub> - (-1)                            | 9.66E-19    | 0      |
| CuCl <sub>2</sub> AQ                                | 1.85E-13    | 0      |
| CuCl <sub>4</sub> -2 1 (-2)                         | 6.39E-24    | 0      |
| CuCl + (+1)   | 2.85E-10    | 0      |
| CuCO <sub>3</sub> AQ                                | 8.57E-08    | 3.3    |
| Cu(CO <sub>3</sub> ) <sub>2</sub> -2 (-2)           | 3.85E-11    | 0      |
| CuSO <sub>4</sub> AQ                                | 5.08E-09    | 0      |
| ATACAMITE   | 0.0148      | *****  |
| AZURITE   | 0.00306     | *****  |
| MALACHITE   | 0.275       | *****  |
| TENORITE  | 2.7         | *****  |
| CU(OH) <sub>2</sub>                                 | 0.258       | *****  |
| CUPRICFERIT   | 0.0117      | *****  |
| CU <sub>2</sub> (OH) <sub>3</sub> NO <sub>3</sub>   | 0.00000437  | *****  |
| ANTLERITE   | 0.000634    | *****  |
| CUOCUSO <sub>4</sub>                                | 1.45E-14    | *****  |
| BROCHANTITE   | 0.00406     | *****  |
| LANGITE   | 0.000463    | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ,3W | 3.4E-11     | *****  |
| CHALCANTHITE  | 0.00000001  | *****  |
| MELANOTHALLI  | 2.52E-17    | *****  |
| CUCO <sub>3</sub>                                   | 0.000068    | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>     | 1.83E-09    | *****  |
| CUSO <sub>4</sub>                                   | 4E-14       | *****  |

MINEQL output for speciation of copper without considering contribution from sediment

Locatin 3 (Intermediate Period), Dhanmondi Lake

| Name  | Conc.       | %Total |
|---|-------------|--------|
| Cu(2+)  | 0.000000252 | 8.4    |
| Cu <sub>2</sub> (OH) <sub>2</sub> +2 (+2)           | 5.41E-10    | 0      |
| Cu(OH) <sub>3</sub> - (-1)                          | 2.53E-12    | 0      |
| Cu(OH) <sub>4</sub> -2 (-2)                         | 1.39E-17    | 0      |
| CuOH + (+1)   | 4.28E-08    | 1.4    |
| Cu(OH) <sub>2</sub> AQ                              | 0.00000179  | 59.5   |
| CuHCO <sub>3</sub> + (+1)                           | 9.22E-09    | 0      |
| CuHPO <sub>4</sub>                                  | 6.2E-10     | 0      |
| Fe(st)OCu (+1)                                      | 3.77E-08    | 1.3    |
| *Fe(wk)OCu (+1)                                     | 0.000000755 | 25.2   |
| CuCl <sub>3</sub> - (-1)                            | 2.28E-18    | 0      |
| CuCl <sub>2</sub> AQ                                | 4.32E-13    | 0      |
| CuCl <sub>4</sub> -2 1 (-2)                         | 2.65E-23    | 0      |
| CuCl + (+1)   | 6.13E-10    | 0      |
| CuCO <sub>3</sub> AQ                                | 9.88E-08    | 3.3    |
| Cu(CO <sub>3</sub> ) <sub>2</sub> -2 (-2)           | 1.73E-11    | 0      |
| CuSO <sub>4</sub> AQ                                | 1.57E-08    | 0      |
| ATACAMITE   | 0.0129      | *****  |
| AZURITE   | 0.00113     | *****  |
| MALACHITE   | 0.145       | *****  |
| TENORITE  | 1.26        | *****  |
| CU(OH) <sub>2</sub>                                 | 0.121       | *****  |
| CUPRICFERIT   | 0.00863     | *****  |
| CU <sub>2</sub> (OH) <sub>3</sub> NO <sub>3</sub>   | 0.00000338  | *****  |
| ANTLERITE   | 0.00299     | *****  |
| CUOCUSO <sub>4</sub>                                | 6.52E-15    | *****  |
| BROCHANTITE   | 0.0228      | *****  |
| LANGITE   | 0.00023     | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ,3W | 2.73E-09    | *****  |
| CHALCANTHITE  | 3.65E-08    | *****  |
| MELANOTHALLI  | 5.27E-17    | *****  |
| CUCO <sub>3</sub>                                   | 0.0000785   | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>     | 0.000000147 | *****  |
| CUSO <sub>4</sub>                                   | 4.39E-14    | *****  |

MINEQL output for speciation of copper without considering contribution of sediment

| Name  |  | Conc.       | %Total |
|---|--|-------------|--------|
| Cu(2+)  |  | 6.39E-08    | 1.8    |
| Cu <sub>2</sub> (OH) <sub>2</sub> +2 (+2)           |  | 6.66E-10    | 0      |
| Cu(OH) <sub>3</sub> - (-1)                          |  | 1.01E-11    | 0      |
| Cu(OH) <sub>4</sub> -2 (-2)                         |  | 1.45E-16    | 0      |
| CuOH + (+1)   |  | 2.68E-08    | 0      |
| Cu(OH) <sub>2</sub> AQ                              |  | 0.00000281  | 77.9   |
| CuHCO <sub>3</sub> + (+1)                           |  | 5.96E-09    | 0      |
| CuHPO <sub>4</sub>                                  |  | 2.09E-11    | 0      |
| Fe(st)OCu (+1)                                      |  | 2.99E-08    | 0      |
| *Fe(wk)OCu (+1)                                     |  | 0.000000501 | 13.9   |
| CuCl <sub>3</sub> - (-1)                            |  | 5.92E-18    | 0      |
| CuCl <sub>2</sub> AQ                                |  | 5.57E-13    | 0      |
| CuCl <sub>2</sub> -2 1 (-2)                         |  | 7.88E-23    | 0      |
| CuCl + (+1)   |  | 4.31E-10    | 0      |
| CuCO <sub>3</sub> AQ                                |  | 0.000000161 | 4.5    |
| Cu(CO <sub>3</sub> ) <sub>2</sub> -2 (-2)           |  | 1.93E-10    | 0      |
| CuSO <sub>4</sub> AQ                                |  | 4.27E-09    | 0      |
| ATACAMITE   |  | 0.0685      | *****  |
| AZURITE   |  | 0.0217      | *****  |
| MALACHITE   |  | 1.01        | *****  |
| TENORITE  |  | 5.31        | *****  |
| CU(OH) <sub>2</sub>                                 |  | 0.507       | *****  |
| CUPRICFERIT   |  | 0.0225      | *****  |
| CU <sub>2</sub> (OH) <sub>3</sub> NO <sub>3</sub>   |  | 0.0000101   | *****  |
| ANTLERITE   |  | 0.00186     | *****  |
| CUOCUSO <sub>4</sub>                                |  | 2.55E-14    | *****  |
| BROCHANTITE   |  | 0.0222      | *****  |
| LANGITE   |  | 0.00288     | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ,3W |  | 4.88E-12    | *****  |
| CHALCANTHITE  |  | 8.36E-09    | *****  |
| MELANOTHALLI  |  | 7.61E-17    | *****  |
| CUCO <sub>3</sub>                                   |  | 0.000127    | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>     |  | 2.62E-10    | *****  |
| CUSO <sub>4</sub>                                   |  | 3.55E-14    | *****  |

MINEQL output for speciation of copper without considering contribution of sediment

Location 4 (Wet Period), Dhanmondi Lake

| Name  | Conc.       | %Total |
|---|-------------|--------|
| Cu(2+)  | 0.000000137 | 4.7    |
| Cu <sub>2</sub> (OH) <sub>2</sub> +2 (+2)           | 6.85E-10    | 0      |
| Cu(OH) <sub>3</sub> - (-1)                          | 2.74E-12    | 0      |
| Cu(OH) <sub>4</sub> -2 (-2)                         | 1.9E-17     | 0      |
| CuOH + (+1)   | 2.93E-08    | 1      |
| Cu(OH) <sub>2</sub> AQ                              | 0.00000154  | 52.9   |
| CuHCO <sub>3</sub> + (+1)                           | 6.49E-09    | 0      |
| CuHPO <sub>4</sub>                                  | 1.37E-10    | 0      |
| Fe(st)OCu (+1)                                      | 5.83E-08    | 2      |
| *Fe(wk)OCu (+1)                                     | 0.00000104  | 35.7   |
| CuCl <sub>3</sub> - (-1)                            | 1.13E-18    | 0      |
| CuCl <sub>2</sub> AQ                                | 2.39E-13    | 0      |
| CuCl <sub>4</sub> -2 1 (-2)                         | 7.07E-24    | 0      |
| CuCl + (+1)   | 4.07E-10    | 0      |
| CuCO <sub>3</sub> AQ                                | 8.75E-08    | 3      |
| Cu(CO <sub>3</sub> ) <sub>2</sub> -2 (-2)           | 2.52E-11    | 0      |
| CuSO <sub>4</sub> AQ                                | 7.93E-09    | 0      |
| ATACAMITE   | 0.0164      | *****  |
| AZURITE   | 0.00295     | *****  |
| MALACHITE   | 0.268       | *****  |
| TENORITE  | 2.58        | *****  |
| CU(OH) <sub>2</sub>                                 | 0.247       | *****  |
| CUPRICFERIT   | 0.0116      | *****  |
| CU <sub>2</sub> (OH) <sub>3</sub> NO <sub>3</sub>   | 0.00000531  | *****  |
| ANTLERITE   | 0.00104     | *****  |
| CUOCUSO <sub>4</sub>                                | 1.99E-14    | *****  |
| BROCHANTITE   | 0.00683     | *****  |
| LANGITE   | 0.000655    | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> .3W | 1.15E-10    | *****  |
| CHALCANTHITE  | 1.59E-08    | *****  |
| MELANOTHALLI  | 3.22E-17    | *****  |
| CUCO <sub>3</sub>                                   | 0.0000695   | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>     | 6.19E-09    | *****  |
| CUSO <sub>4</sub>                                   | 5.8E-14     | *****  |



MINEQL output for speciation of copper without considering contribution of sediment

Location 4 (Intermediate Period), Dhanmondi Lake

| Name  | Conc.       | %Total |
|---|-------------|--------|
| Cu(2+)  | 4.16E-10    | 0      |
| Cu <sub>2</sub> (OH) <sub>2</sub> +2 (+2)           | 1.04E-12    | 0      |
| Cu(OH) <sub>3</sub> - (-1)                          | 6.62E-11    | 0      |
| Cu(OH) <sub>4</sub> -2 (-2)                         | 8.88E-15    | 0      |
| CuOH + (+1)   | 1.8E-09     | 0      |
| Cu(OH) <sub>2</sub> AQ                              | 0.00000188  | 78.5   |
| CuHCO <sub>3</sub> + (+1)                           | 3.88E-10    | 0      |
| CuHPO <sub>4</sub>                                  | 5.24E-12    | 0      |
| Fe(st)OCu (+1)                                      | 2.97E-08    | 1.2    |
| *Fe(wk)OCu (+1)                                     | 0.000000367 | 15.3   |
| CuCl <sub>3</sub> - (-1)                            | 5.42E-21    | 0      |
| CuCl <sub>2</sub> AQ                                | 9.3E-16     | 0      |
| CuCl <sub>4</sub> -2 1 (-2)                         | 6.53E-26    | 0      |
| CuCl + (+1)   | 1.19E-12    | 0      |
| CuCO <sub>3</sub> AQ                                | 0.000000105 | 4.4    |
| Cu(CO <sub>3</sub> ) <sub>2</sub> -2 (-2)           | 1.11E-08    | 0      |
| CuSO <sub>4</sub> AQ                                | 2.83E-11    | 0      |
| ATACAMITE   | 0.000702    | *****  |
| AZURITE   | 0.00154     | *****  |
| MALACHITE   | 0.177       | *****  |
| TENORITE  | 1.46        | *****  |
| CU(OH) <sub>2</sub>                                 | 0.139       | *****  |
| CUPRICFERIT   | 0.00953     | *****  |
| CU <sub>2</sub> (OH) <sub>3</sub> NO <sub>3</sub>   | 0.000000168 | *****  |
| ANTLERITE   | 0.00000597  | *****  |
| CUOCUSO <sub>4</sub>                                | 1.52E-17    | *****  |
| BROCHANTITE   | 0.000048    | *****  |
| LANGITE   | 0.000000812 | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ,3W | 2.06E-13    | *****  |
| CHALCANTHITE  | 6.49E-11    | *****  |
| MELANOTHALLI  | 1.15E-19    | *****  |
| CUCO <sub>3</sub>                                   | 0.000083    | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>     | 1.11E-11    | *****  |
| CUSO <sub>4</sub>                                   | 8.75E-17    | *****  |

MINEQL output for speciation of copper without considering contribution of sediment

Location 5 (Dry Period), Dhanmondi Lake

| Name  | Conc.       | %Total |
|---|-------------|--------|
| Cu(2+)  | 0.00000003  | 0      |
| Cu <sub>2</sub> (OH) <sub>2</sub> +2 (+2)           | 3.63E-10    | 0      |
| Cu(OH) <sub>3</sub> - (-1)                          | 1.65E-11    | 0      |
| Cu(OH) <sub>4</sub> -2 (-2)                         | 3.5E-16     | 0      |
| CuOH + (+1)   | 1.92E-08    | 0      |
| Cu(OH) <sub>2</sub> AQ                              | 0.00000304  | 78.1   |
| CuHCO <sub>3</sub> + (+1)                           | 4.28E-09    | 0      |
| CuHPO <sub>4</sub>                                  | 7.14E-12    | 0      |
| Fe(st)OCu (+1)                                      | 0.000000039 | 0      |
| *Fe(wk)OCu (+1)                                     | 0.000000585 | 15     |
| CuCl <sub>3</sub> - (-1)                            | 2.03E-18    | 0      |
| CuCl <sub>2</sub> AQ                                | 2.16E-13    | 0      |
| CuCl <sub>4</sub> -2 1 (-2)                         | 2.3E-23     | 0      |
| CuCl + (+1)   | 1.87E-10    | 0      |
| CuCO <sub>3</sub> AQ                                | 0.000000175 | 4.5    |
| Cu(CO <sub>3</sub> ) <sub>2</sub> -2 (-2)           | 4.69E-10    | 0      |
| CuSO <sub>4</sub> AQ                                | 1.76E-09    | 0      |
| ATACAMITE   | 0.0507      | *****  |
| AZURITE   | 0.0305      | *****  |
| MALACHITE   | 1.27        | *****  |
| TENORITE  | 6.1         | *****  |
| CU(OH) <sub>2</sub>                                 | 0.583       | *****  |
| CUPRICFERIT   | 0.0251      | *****  |
| CU <sub>2</sub> (OH) <sub>3</sub> NO <sub>3</sub>   | 0.00000838  | *****  |
| ANTLERITE   | 0.000895    | *****  |
| CUOCUSO <sub>4</sub>                                | 1.3E-14     | *****  |
| BROCHANTITE   | 0.0116      | *****  |
| LANGITE   | 0.00176     | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ,3W | 6.17E-13    | *****  |
| CHALCANTHITE  | 3.41E-09    | *****  |
| MELANOTHALLI  | 2.96E-17    | *****  |
| CUCO <sub>3</sub>                                   | 0.000139    | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>     | 3.31E-11    | *****  |
| CUSO <sub>4</sub>                                   | 1.56E-14    | *****  |

MINEQL output for speciation of copper without considering contribution of sediment

Location 5 (Wet Period), Dhanmondi Lake

| Name  | Conc.       | %Total |
|---|-------------|--------|
| Cu(2+)  | 9.56E-09    | 0      |
| Cu <sub>2</sub> (OH) <sub>2</sub> +2 (+2)           | 5.78E-11    | 0      |
| Cu(OH) <sub>3</sub> - (-1)                          | 1.21E-11    | 0      |
| Cu(OH) <sub>4</sub> -2 (-2)                         | 3.36E-16    | 0      |
| CuOH + (+1)   | 8.08E-09    | 0      |
| Cu(OH) <sub>2</sub> AQ                              | 0.00000169  | 52.8   |
| CuHCO <sub>3</sub> + (+1)                           | 1.8E-09     | 0      |
| CuHPO <sub>4</sub>                                  | 1.27E-12    | 0      |
| Fe(st)OCu (+1)                                      | 0.000000111 | 3.5    |
| *Fe(wk)OCu (+1)                                     | 0.00000128  | 40.1   |
| CuCl <sub>3</sub> - (-1)                            | 8.59E-20    | 0      |
| CuCl <sub>2</sub> AQ                                | 1.77E-14    | 0      |
| CuCl <sub>4</sub> -2 1 (-2)                         | 5.27E-25    | 0      |
| CuCl + (+1)   | 2.97E-11    | 0      |
| CuCO <sub>3</sub> AQ                                | 9.65E-08    | 3      |
| Cu(CO <sub>3</sub> ) <sub>2</sub> -2 (-2)           | 4.47E-10    | 0      |
| CuSO <sub>4</sub> AQ                                | 4.59E-10    | 0      |
| ATACAMITE   | 0.00554     | *****  |
| AZURITE   | 0.00449     | *****  |
| MALACHITE   | 0.354       | *****  |
| TENORITE  | 3.09        | *****  |
| CU(OH) <sub>2</sub>                                 | 0.295       | *****  |
| CUPRICFERIT   | 0.0133      | *****  |
| CU <sub>2</sub> (OH) <sub>3</sub> NO <sub>3</sub>   | 0.00000177  | *****  |
| ANTLERITE   | 0.0000726   | *****  |
| CUOCUSO <sub>4</sub>                                | 1.53E-15    | *****  |
| BROCHANTITE   | 0.000523    | *****  |
| LANGITE   | 0.0000622   | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> .3W | 1.08E-14    | *****  |
| CHALCANTHITE  | 9.04E-10    | *****  |
| MELANOTHALLI  | 2.41E-18    | *****  |
| CUCO <sub>3</sub>                                   | 0.0000767   | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>     | 5.83E-13    | *****  |
| CUSO <sub>4</sub>                                   | 3.68E-15    | *****  |

MINEQL output for speciation of copper without considering contribution of sediment

Location 5 (Intermediate Period), Dhanmondi Lake

| Name  | Conc.       | %Total |
|---|-------------|--------|
| Cu(2+)  | 5.02E-09    | 0      |
| Cu <sub>2</sub> (OH) <sub>2</sub> +2 (+2)           | 8.48E-12    | 0      |
| Cu(OH) <sub>3</sub> - (-1)                          | 1.26E-11    | 0      |
| Cu(OH) <sub>4</sub> -2 (-2)                         | 4.42E-16    | 0      |
| CuOH + (+1)   | 5.35E-09    | 0      |
| Cu(OH) <sub>2</sub> AQ                              | 0.00000141  | 70.3   |
| CuHCO <sub>3</sub> + (+1)                           | 1.15E-09    | 0      |
| CuHPO <sub>4</sub>                                  | 9.39E-13    | 0      |
| Fe(st)OCu (+1)                                      | 4.23E-08    | 2.1    |
| *Fe(wk)OCu (+1)                                     | 0.000000461 | 23     |
| CuCl <sub>3</sub> - (-1)                            | 4.46E-20    | 0      |
| CuCl <sub>2</sub> AQ                                | 8.46E-15    | 0      |
| CuCl <sub>4</sub> -2 1 (-2)                         | 5.22E-25    | 0      |
| CuCl + (+1)   | 1.21E-11    | 0      |
| CuCO <sub>3</sub> AQ                                | 7.78E-08    | 3.9    |
| Cu(CO <sub>3</sub> ) <sub>2</sub> -2 (-2)           | 5.51E-10    | 0      |
| CuSO <sub>4</sub> AQ                                | 2.6E-10     | 0      |
| ATACAMITE   | 0.00126     | *****  |
| AZURITE   | 0.000553    | *****  |
| MALACHITE   | 0.09        | *****  |
| TENORITE  | 0.996       | *****  |
| CU(OH) <sub>2</sub>                                 | 0.0951      | *****  |
| CUPRICFERIT   | 0.00679     | *****  |
| CU <sub>2</sub> (OH) <sub>3</sub> NO <sub>3</sub>   | 0.000000331 | *****  |
| ANTLERITE   | 0.0000308   | *****  |
| CUOCUSO <sub>4</sub>                                | 8.51E-17    | *****  |
| BROCHANTITE   | 0.000185    | *****  |
| LANGITE   | 0.00000187  | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ,3W | 4.94E-15    | *****  |
| CHALCANTHITE  | 6.05E-10    | *****  |
| MELANOTHALLI  | 1.03E-18    | *****  |
| CUCO <sub>3</sub>                                   | 0.0000618   | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>     | 2.65E-13    | *****  |
| CUSO <sub>4</sub>                                   | 7.28E-16    | *****  |



MINEQL output for speciation of copper without considering contribution from sediment

Location 6(Dry Period),Dhanmondi Lake

| Name  | Conc.       | %Total |
|---|-------------|--------|
| Cu(2+)  | 4.38E-08    | 1.2    |
| Cu <sub>2</sub> (OH) <sub>2</sub> +2 (+2)           | 5.12E-10    | 0      |
| Cu(OH) <sub>3</sub> - (-1)                          | 1.39E-11    | 0      |
| Cu(OH) <sub>4</sub> -2 (-2)                         | 2.5E-16     | 0      |
| CuOH + (+1)   | 2.31E-08    | 0      |
| Cu(OH) <sub>2</sub> AQ                              | 0.00000305  | 84.7   |
| CuHCO <sub>3</sub> + (+1)                           | 5.15E-09    | 0      |
| CuHPO <sub>4</sub>                                  | 9.94E-12    | 0      |
| Fe(st)OCu (+1)                                      | 5.28E-09    | 0      |
| *Fe(wk)OCu (+1)                                     | 0.000000296 | 8.2    |
| CuCl <sub>3</sub> - (-1)                            | 6.89E-18    | 0      |
| CuCl <sub>2</sub> AQ                                | 5.45E-13    | 0      |
| CuCl <sub>4</sub> -2 1 (-2)                         | 1.08E-22    | 0      |
| CuCl + (+1)   | 3.55E-10    | 0      |
| CuCO <sub>3</sub> AQ                                | 0.000000175 | 4.8    |
| Cu(CO <sub>3</sub> ) <sub>2</sub> -2 (-2)           | 3.34E-10    | 0      |
| CuSO <sub>4</sub> AQ                                | 0.000000002 | 0      |
| ATACAMITE   | 0.0784      | *****  |
| AZURITE   | 0.029       | *****  |
| MALACHITE   | 1.23        | *****  |
| TENORITE  | 5.91        | *****  |
| CU(OH) <sub>2</sub>                                 | 0.565       | *****  |
| CUPRICFERIT   | 0.0247      | *****  |
| CU <sub>2</sub> (OH) <sub>3</sub> NO <sub>3</sub>   | 0.00000964  | *****  |
| ANTLERITE   | 0.00103     | *****  |
| CUOCUSO <sub>4</sub>                                | 1.38E-14    | *****  |
| BROCHANTITE   | 0.0134      | *****  |
| LANGITE   | 0.00185     | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ,3W | 1.2E-12     | *****  |
| CHALCANTHITE  | 3.91E-09    | *****  |
| MELANOTHALLI  | 7.46E-17    | *****  |
| CUCO <sub>3</sub>                                   | 0.000139    | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>     | 6.44E-11    | *****  |
| CUSO <sub>4</sub>                                   | 1.72E-14    | *****  |

MINEQL output for speciation of copper without considering contribution of sediment

Location 6 (Wet Period), Dhanmondi Lake

| Name  | Conc.       | %Total |
|---|-------------|--------|
| Cu(2+)  | 6.39E-08    | 2      |
| Cu <sub>2</sub> (OH) <sub>2</sub> +2 (+2)           | 4.13E-10    | 0      |
| Cu(OH) <sub>3</sub> - (-1)                          | 5.09E-12    | 0      |
| Cu(OH) <sub>4</sub> -2 (-2)                         | 5.54E-17    | 0      |
| CuOH + (+1)   | 2.17E-08    | 0      |
| Cu(OH) <sub>2</sub> AQ                              | 0.00000181  | 56.4   |
| CuHCO <sub>3</sub> + (+1)                           | 4.83E-09    | 0      |
| CuHPO <sub>4</sub>                                  | 5.11E-11    | 0      |
| Fe(st)OCu (+1)                                      | 6.81E-08    | 2.1    |
| *Fe(wk)OCu (+1)                                     | 0.00000113  | 35.2   |
| CuCl <sub>3</sub> - (-1)                            | 8.49E-19    | 0      |
| CuCl <sub>2</sub> AQ                                | 1.55E-13    | 0      |
| CuCl <sub>4</sub> -2 1 (-2)                         | 5.83E-24    | 0      |
| CuCl + (+1)   | 2.28E-10    | 0      |
| CuCO <sub>3</sub> AQ                                | 0.000000103 | 3.2    |
| Cu(CO <sub>3</sub> ) <sub>2</sub> -2 (-2)           | 7.37E-11    | 0      |
| CuSO <sub>4</sub> AQ                                | 4.5E-09     | 0      |
| ATACAMITE   | 0.0181      | *****  |
| AZURITE   | 0.00549     | *****  |
| MALACHITE   | 0.405       | *****  |
| TENORITE  | 3.3         | *****  |
| CU(OH) <sub>2</sub>                                 | 0.316       | *****  |
| CUPRICFERIT   | 0.0142      | *****  |
| CU <sub>2</sub> (OH) <sub>3</sub> NO <sub>3</sub>   | 0.00000512  | *****  |
| ANTLERITE   | 0.000814    | *****  |
| CUOCUSO <sub>4</sub>                                | 1.61E-14    | *****  |
| BROCHANTITE   | 0.00627     | *****  |
| LANGITE   | 0.000746    | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ,3W | 1.88E-11    | *****  |
| CHALCANTHITE  | 8.88E-09    | *****  |
| MELANOTHALLI  | 2.11E-17    | *****  |
| CUCO <sub>3</sub>                                   | 0.000082    | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>     | 1.01E-09    | *****  |
| CUSO <sub>4</sub>                                   | 3.62E-14    | *****  |

MINEQL output for speciation of copper without considering contribution from sediment

Location 8(Intermediate Period),Dhanmondi Lake

| Name   | Conc.       | %Total |
|--|-------------|--------|
| Cu(2+)   | 0.000000242 | 10.5   |
| Cu <sub>2</sub> (OH) <sub>2</sub> <sup>2+</sup> (+2) | 5.19E-10    | 0      |
| Cu(OH) <sub>3</sub> <sup>-</sup> (-1)                | 2.42E-12    | 0      |
| Cu(OH) <sub>4</sub> <sup>-2</sup> (-2)               | 1.35E-17    | 0      |
| CuOH <sup>+</sup> (+1)                               | 4.07E-08    | 1.8    |
| Cu(OH) <sub>2</sub> AQ                               | 0.0000017   | 73.7   |
| CuHCO <sub>3</sub> <sup>+</sup> (+1)                 | 8.77E-09    | 0      |
| CuHPO <sub>4</sub>                                   | 4.05E-11    | 0      |
| Fe(st)OCu (+1)                                       | 2.25E-09    | 0      |
| *Fe(wk)OCu (+1)                                      | 0.0000002   | 8.7    |
| CuCl <sub>3</sub> <sup>-</sup> (-1)                  | 2.42E-18    | 0      |
| CuCl <sub>2</sub> AQ                                 | 4.41E-13    | 0      |
| CuCl <sub>4</sub> <sup>-2</sup> 1 (-2)               | 2.87E-23    | 0      |
| CuCl <sup>+</sup> (+1)                               | 6.09E-10    | 0      |
| CuCO <sub>3</sub> AQ                                 | 9.39E-08    | 4.1    |
| Cu(CO <sub>3</sub> ) <sub>2</sub> <sup>-2</sup> (-2) | 1.69E-11    | 0      |
| CuSO <sub>4</sub> AQ                                 | 1.41E-08    | 0      |
| ATACAMITE  | 0.0126      | *****  |
| AZURITE  | 0.00104     | *****  |
| MALACHITE  | 0.137       | *****  |
| TENORITE   | 1.26        | *****  |
| CU(OH) <sub>2</sub>                                  | 0.12        | *****  |
| CUPRICFERIT  | 0.00838     | *****  |
| CU <sub>2</sub> (OH) <sub>3</sub> NO <sub>3</sub>    | 0.00000318  | *****  |
| ANTLERITE  | 0.00242     | *****  |
| CUOCUSO <sub>4</sub>                                 | 6.17E-15    | *****  |
| BROCHANTITE  | 0.0175      | *****  |
| LANGITE  | 0.000199    | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ,3W  | 1.11E-11    | *****  |
| CHALCANTHITE   | 3.26E-08    | *****  |
| MELANOTHALLI   | 5.4E-17     | *****  |
| CUCO <sub>3</sub>                                    | 0.0000746   | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>      | 5.95E-10    | *****  |
| CUSO <sub>4</sub>                                    | 4.15E-14    | *****  |

MINEQL output for speciation of copper without considering contribution of sediment

Location 7 (Dry Period), Dhanmondi Lake

| Name   | Conc.       | %Total |
|--|-------------|--------|
| Cu(2+)   | 2.25E-08    | 0      |
| Cu <sub>2</sub> (OH) <sub>2</sub> <sup>2+</sup> (+2) | 2.6E-10     | 0      |
| Cu(OH) <sub>3</sub> <sup>-</sup> (-1)                | 1.88E-11    | 0      |
| Cu(OH) <sub>4</sub> <sup>-2</sup> (-2)               | 4.66E-16    | 0      |
| CuOH <sup>+</sup> (+1)                               | 1.64E-08    | 0      |
| Cu(OH) <sub>2</sub> AQ                               | 0.00000298  | 60.9   |
| CuHCO <sub>3</sub> <sup>+</sup> (+1)                 | 3.65E-09    | 0      |
| CuHPO <sub>4</sub>                                   | 3.98E-12    | 0      |
| Fe(st)OCu (+1)                                       | 0.000000113 | 2.3    |
| *Fe(wk)OCu (+1)                                      | 0.00000159  | 32.4   |
| CuCl <sub>3</sub> <sup>-</sup> (-1)                  | 6.2E-18     | 0      |
| CuCl <sub>2</sub> AQ                                 | 4.07E-13    | 0      |
| CuCl <sub>4</sub> <sup>-2</sup> 1 (-2)               | 1.17E-22    | 0      |
| CuCl <sup>+</sup> (+1)                               | 2.2E-10     | 0      |
| CuCO <sub>3</sub> AQ                                 | 0.000000171 | 3.5    |
| Cu(CO <sub>3</sub> ) <sub>2</sub> <sup>-2</sup> (-2) | 6.24E-10    | 0      |
| CuSO <sub>4</sub> AQ                                 | 1.14E-09    | 0      |
| ATACAMITE  | 0.0661      | *****  |
| AZURITE  | 0.0276      | *****  |
| MALACHITE  | 1.19        | *****  |
| TENORITE   | 5.83        | *****  |
| CU(OH) <sub>2</sub>                                  | 0.557       | *****  |
| CUPRICFERIT  | 0.0243      | *****  |
| CU <sub>2</sub> (OH) <sub>3</sub> NO <sub>3</sub>    | 0.00000674  | *****  |
| ANTLERITE  | 0.000557    | *****  |
| CUOCUSO <sub>4</sub>                                 | 7.78E-15    | *****  |
| BROCHANTITE  | 0.00709     | *****  |
| LANGITE  | 0.001       | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ,3W  | 1.88E-13    | *****  |
| CHALCANTHITE   | 2.21E-09    | *****  |
| MELANOTHALLI   | 5.57E-17    | *****  |
| CUCO <sub>3</sub>                                    | 0.000136    | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>      | 1.01E-11    | *****  |
| CUSO <sub>4</sub>                                    | 9.81E-15    | *****  |



MINEQL output for speciation of copper without considering contribution of sediment

Location 7 (Wet period), Dhanmondi Lake

| Name            | Conc.       | %Total |
|-----------------|-------------|--------|
| Cu(2+)          | 0.00000014  | 0      |
| Cu2(OH)2+2 (+2) | 7.92E-11    | 0      |
| Cu(OH)3 - (-1)  | 8.85E-12    | 0      |
| Cu(OH)4 -2 (-2) | 1.9E-16     | 0      |
| CuOH + (+1)     | 9.53E-09    | 0      |
| Cu(OH)2 AQ      | 0.00000158  | 46.5   |
| CuHCO3 + (+1)   | 2.12E-09    | 0      |
| CuHPO4          | 5.12E-12    | 0      |
| Fe(st)OCu (+1)  | 0.000000128 | 3.8    |
| *Fe(wk)OCu (+1) | 0.00000157  | 46.3   |
| CuCl3 - (-1)    | 2.09E-18    | 0      |
| CuCl2 AQ        | 1.71E-13    | 0      |
| CuCl -2 1 (-2)  | 3.18E-23    | 0      |
| CuCl + (+1)     | 1.13E-10    | 0      |
| CuCO3 AQ        | 9.04E-08    | 2.7    |
| Cu(CO3)2-2 (-2) | 2.53E-10    | 0      |
| CuSO4 AQ        | 1.69E-10    | 0      |
| ATACAMITE       | 0.0156      | *****  |
| AZURITE         | 0.00369     | *****  |
| MALACHITE       | 0.311       | *****  |
| TENORITE        | 2.89        | *****  |
| CU(OH)2         | 0.276       | *****  |
| CUPRICFERIT     | 0.0125      | *****  |
| CU2(OH)3NO3     | 0.00000198  | *****  |
| ANTLERITE       | 0.0000235   | *****  |
| CUOCUSO4        | 5.29E-16    | *****  |
| BROCHANTITE     | 0.000158    | *****  |
| LANGITE         | 0.0000188   | *****  |
| CU3(PO4)2,3W    | 1.65E-13    | *****  |
| CHALCANTHITE    | 3.33E-10    | *****  |
| MELANOTHALLI    | 2.33E-17    | *****  |
| CUCO3           | 0.0000718   | *****  |
| CU3(PO4)2       | 8.86E-12    | *****  |
| CUSO4           | 1.36E-15    | *****  |

MINEQL output for speciation of copper without considering contribution of sediment

Location 7 (Intermediate Period), Dhanmondi Lake

| Name  | Conc.       | %Total |
|---|-------------|--------|
| Cu(2+)  | 3.24E-09    | 0      |
| Cu <sub>2</sub> (OH) <sub>2</sub> +2 (+2)           | 9.66E-12    | 0      |
| Cu(OH) <sub>3</sub> - (-1)                          | 3.25E-11    | 0      |
| Cu(OH) <sub>4</sub> -2 (-2)                         | 1.68E-15    | 0      |
| CuOH + (+1)   | 5.66E-09    | 0      |
| Cu(OH) <sub>2</sub> AQ                              | 0.00000236  | 67.4   |
| CuHCO <sub>3</sub> + (+1)                           | 1.22E-09    | 0      |
| CuHPO <sub>4</sub>                                  | 9.69E-13    | 0      |
| Fe(st)OCu (+1)                                      | 7.82E-08    | 2.2    |
| *Fe(wk)OCu (+1)                                     | 0.000000919 | 26.2   |
| CuCl <sub>3</sub> - (-1)                            | 5.04E-28    | 0      |
| CuCl <sub>2</sub> AQ                                | 3.83E-20    | 0      |
| CuCl <sub>2</sub> -2 1 (-2)                         | 1.39E-35    | 0      |
| CuCl + (+1)   | 2.12E-14    | 0      |
| CuCO <sub>3</sub> AQ                                | 0.000000131 | 3.7    |
| Cu(CO <sub>3</sub> ) <sub>2</sub> -2 (-2)           | 2.1E-09     | 0      |
| CuSO <sub>4</sub> AQ                                | 1.36E-10    | 0      |
| ATACAMITE   | 0.00000607  | *****  |
| AZURITE   | 0.00281     | *****  |
| MALACHITE   | 0.265       | *****  |
| TENORITE  | 1.75        | *****  |
| CU(OH) <sub>2</sub>                                 | 0.167       | *****  |
| CUPRICFERIT   | 0.0117      | *****  |
| CU <sub>2</sub> (OH) <sub>3</sub> NO <sub>3</sub>   | 0.00000064  | *****  |
| ANTLERITE   | 0.0000452   | *****  |
| CUOCUSO <sub>4</sub>                                | 8.26E-17    | *****  |
| BROCHANTITE   | 0.000455    | *****  |
| LANGITE   | 0.00000516  | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ,3W | 8.82E-15    | *****  |
| CHALCANTHITE  | 3.14E-10    | *****  |
| MELANOTHALLI  | 4.69E-24    | *****  |
| CUCO <sub>3</sub>                                   | 0.000104    | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>     | 4.74E-13    | *****  |
| CUSO <sub>4</sub>                                   | 4E-16       | *****  |

Mineql output for speciation of copper without considering contribution from sediment

Location 1 (Dry Period), Ramna Lake

| Name  | Conc.       | %Total |
|---|-------------|--------|
| Cu(2+)  | 5.87E-10    | 0      |
| Cu <sub>2</sub> (OH) <sub>2</sub> +2 (+2)           | 8.72E-12    | 0      |
| Cu(OH) <sub>3</sub> - (-1)                          | 9.32E-11    | 0      |
| Cu(OH) <sub>4</sub> -2 (-2)                         | 1.19E-14    | 0      |
| CuOH + (+1)   | 2.6E-09     | 0      |
| Cu(OH) <sub>2</sub> AQ                              | 0.00000272  | 77.6   |
| CuHCO <sub>3</sub> + (+1)                           | 5.85E-10    | 0      |
| CuHPO <sub>4</sub>                                  | 8.44E-13    | 0      |
| Fe(st)OCu (+1)                                      | 4.71E-08    | 1.3    |
| *Fe(wk)OCu (+1)                                     | 0.000000558 | 15.9   |
| CuCl <sub>3</sub> - (-1)                            | 1.08E-20    | 0      |
| CuCl <sub>2</sub> AQ                                | 1.9E-15     | 0      |
| CuCl <sub>4</sub> -2 1 (-2)                         | 5.98E-26    | 0      |
| CuCl + (+1)   | 2.67E-12    | 0      |
| CuCO <sub>3</sub> AQ                                | 0.000000157 | 4.5    |
| Cu(CO <sub>3</sub> ) <sub>2</sub> -2 (-2)           | 1.63E-08    | 0      |
| CuSO <sub>4</sub> AQ                                | 1.83E-11    | 0      |
| ATACAMITE   | 0.00512     | *****  |
| AZURITE   | 0.0341      | *****  |
| MALACHITE   | 1.36        | *****  |
| TENORITE  | 7.19        | *****  |
| CU(OH) <sub>2</sub>                                 | 0.687       | *****  |
| CUPRICFERIT   | 0.0259      | *****  |
| CU <sub>2</sub> (OH) <sub>3</sub> NO <sub>3</sub>   | 0.000000355 | *****  |
| ANTLERITE   | 0.00000729  | *****  |
| CU <sub>2</sub> CU <sub>2</sub> SO <sub>4</sub>     | 2.26E-16    | *****  |
| BROCHANTITE   | 0.0000845   | *****  |
| LANGITE   | 0.0000262   | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ,3W | 7.72E-15    | *****  |
| CHALCANTHITE  | 3.39E-11    | *****  |
| MELANOTHALLI  | 2.69E-19    | *****  |
| CUCO <sub>3</sub>                                   | 0.000125    | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>     | 4.14E-13    | *****  |
| CUSO <sub>4</sub>                                   | 2.22E-16    | *****  |

MINEQL output for speciation of copper without considering contribution from sediment

Location 1(Wet Period),Ramna Lake

| Name            | Conc.       | %Total |
|-----------------|-------------|--------|
| Cu(2+)          | 0.00000012  | 10     |
| Cu2(OH)2+2 (+2) | 4.64E-10    | 0      |
| Cu(OH)3 - (-1)  | 1.2E-12     | 0      |
| Cu(OH)4 -2 (-2) | 6.58E-18    | 0      |
| CuOH + (+1)     | 2.04E-08    | 1.7    |
| Cu(OH)2 AQ      | 0.000000851 | 71     |
| CuHCO3 + (+1)   | 4.57E-09    | 0      |
| CuHPO4          | 6E-11       | 0      |
| Fe(st)OCu (+1)  | 1.74E-09    | 0      |
| *Fe(wk)OCu (+1) | 0.000000146 | 12.1   |
| CuCl3 - (-1)    | 1.91E-19    | 0      |
| CuCl2 AQ        | 7.23E-14    | 0      |
| CuCl4 -2 1 (-2) | 5.63E-25    | 0      |
| CuCl + (+1)     | 2.23E-10    | 0      |
| CuCO3 AQ        | 0.000000049 | 4.1    |
| Cu(CO3)2-2 (-2) | 8.88E-12    | 0      |
| CuSO4 AQ        | 5.9E-09     | 0      |
| ATACAMITE       | 0.0048      | *****  |
| AZURITE         | 0.000806    | *****  |
| MALACHITE       | 0.112       | *****  |
| TENORITE        | 1.91        | *****  |
| CU(OH)2         | 0.183       | *****  |
| CUPRICFERIT     | 0.00745     | *****  |
| CU2(OH)3NO3     | 0.000000702 | *****  |
| ANTLERITE       | 0.000233    | *****  |
| CUOCUSO4        | 1.58E-14    | *****  |
| BROCHANTITE     | 0.000847    | *****  |
| LANGITE         | 0.000172    | *****  |
| CU3(PO4)2,3W    | 1.22E-11    | *****  |
| CHALCANTHITE    | 1.12E-08    | *****  |
| MELANOTHALLI    | 1.01E-17    | *****  |
| CUCO3           | 0.0000389   | *****  |
| CU3(PO4)2       | 6.55E-10    | *****  |
| CUSO4           | 5.95E-14    | *****  |



MINEQL output for speciation of copper without considering contribution from sediment

Location 1(Intermediate Period),Ramna Lake

| Name  | Conc.       | %Total |
|---|-------------|--------|
| Cu(2+)  | 0.000000456 | 14.2   |
| Cu <sub>2</sub> (OH) <sub>2</sub> +2 (+2)           | 8.26E-10    | 0      |
| Cu(OH) <sub>3</sub> - (-1)                          | 1.15E-12    | 0      |
| Cu(OH) <sub>4</sub> -2 (-2)                         | 3.9E-18     | 0      |
| CuOH + (+1)   | 4.92E-08    | 1.5    |
| Cu(OH) <sub>2</sub> AQ                              | 0.00000129  | 40.5   |
| CuHCO <sub>3</sub> + (+1)                           | 1.06E-08    | 0      |
| CuHPO <sub>4</sub>                                  | 1.8E-09     | 0      |
| Fe(st)OCu (+1)                                      | 6.24E-08    | 2      |
| *Fe(wk)OCu (+1)                                     | 0.00000124  | 38.6   |
| CuCl <sub>3</sub> - (-1)                            | 1.86E-18    | 0      |
| CuCl <sub>2</sub> AQ                                | 4.7E-13     | 0      |
| CuCl <sub>4</sub> -2 1 (-2)                         | 1.5E-23     | 0      |
| CuCl + (+1)   | 8.88E-10    | 0      |
| CuCO <sub>3</sub> AQ                                | 7.19E-08    | 2.2    |
| Cu(CO <sub>3</sub> ) <sub>2</sub> -2 (-2)           | 4.91E-12    | 0      |
| CuSO <sub>4</sub> AQ                                | 1.59E-08    | 0      |
| ATACAMITE   | 0.00935     | *****  |
| AZURITE   | 0.000535    | *****  |
| MALACHITE   | 0.0878      | *****  |
| TENORITE  | 1.05        | *****  |
| CU(OH) <sub>2</sub>                                 | 0.1         | *****  |
| CUPRICFERIT   | 0.0067      | *****  |
| CU <sub>2</sub> (OH) <sub>3</sub> NO <sub>3</sub>   | 0.000000809 | *****  |
| ANTLERITE   | 0.00158     | *****  |
| CUOCUSO <sub>4</sub>                                | 6.47E-15    | *****  |
| BROCHANTITE   | 0.0087      | *****  |
| LANGITE   | 0.000124    | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> .3W | 1.66E-08    | *****  |
| CHALCANTHITE  | 3.61E-08    | *****  |
| MELANOTHALLI  | 5.82E-17    | *****  |
| CUCO <sub>3</sub>                                   | 0.0000571   | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>     | 0.000000894 | *****  |
| CUSO <sub>4</sub>                                   | 5.16E-14    | *****  |

MINEQL output for speciation of copper with considering contribution from sediment

Location 2(Dry Period),Ramna Lake

| Name  | Conc.       | %Total |
|---|-------------|--------|
| Cu(2+)  | 2.38E-10    | 0      |
| Cu <sub>2</sub> (OH) <sub>2</sub> +2 (+2)           | 3.37E-12    | 0      |
| Cu(OH) <sub>3</sub> - (-1)                          | 1.5E-10     | 0      |
| Cu(OH) <sub>4</sub> -2 (-2)                         | 3.17E-14    | 0      |
| CuOH + (+1)   | 1.63E-09    | 0      |
| Cu(OH) <sub>2</sub> AQ                              | 0.00000271  | 82.2   |
| CuHCO <sub>3</sub> + (+1)                           | 3.68E-10    | 0      |
| CuHPO <sub>4</sub>                                  | 8.5E-13     | 0      |
| Fe(st)OCu (+1)                                      | 3.03E-08    | 0      |
| *Fe(wk)OCu (+1)                                     | 0.000000355 | 10.8   |
| CuCl <sub>3</sub> - (-1)                            | 1.61E-21    | 0      |
| CuCl <sub>2</sub> AQ                                | 3.87E-16    | 0      |
| CuCl <sub>4</sub> -2 1 (-2)                         | 6.87E-27    | 0      |
| CuCl + (+1)   | 7.53E-13    | 0      |
| CuCO <sub>3</sub> AQ                                | 0.000000157 | 4.8    |
| Cu(CO <sub>3</sub> ) <sub>2</sub> -2 (-2)           | 4.31E-08    | 1.3    |
| CuSO <sub>4</sub> AQ                                | 1.32E-11    | 0      |
| ATACAMITE   | 0.00222     | *****  |
| AZURITE   | 0.0318      | *****  |
| MALACHITE   | 1.29        | *****  |
| TENORITE  | 6.89        | *****  |
| CU(OH) <sub>2</sub>                                 | 0.658       | *****  |
| CUPRICFERIT   | 0.0253      | *****  |
| CU <sub>2</sub> (OH) <sub>3</sub> NO <sub>3</sub>   | 0.000000209 | *****  |
| ANTLERITE   | 0.00000526  | *****  |
| CUOCUSO <sub>4</sub>                                | 1.49E-16    | *****  |
| BROCHANTITE   | 0.0000608   | *****  |
| LANGITE   | 0.000017    | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ,3W | 7.8E-15     | *****  |
| CHALCANTHITE  | 2.46E-11    | *****  |
| MELANOTHALLI  | 5.46E-20    | *****  |
| CUCO <sub>3</sub>                                   | 0.000125    | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>     | 4.19E-13    | *****  |
| CUSO <sub>4</sub>                                   | 1.53E-16    | *****  |

MINEQL output for speciation of copper without considering contribution from sediment

Location 2(Wet Period), Ramna Lake

| Name            | Conc.       | %Total |
|-----------------|-------------|--------|
| Cu(2+)          | 0.000000189 | 6.8    |
| Cu2(OH)2+2 (+2) | 1.92E-09    | 0      |
| Cu(OH)3 - (-1)  | 3.79E-12    | 0      |
| Cu(OH)4 -2 (-2) | 2.59E-17    | 0      |
| CuOH + (+1)     | 4.06E-08    | 1.5    |
| Cu(OH)2 AQ      | 0.00000213  | 76.2   |
| CuHCO3 + (+1)   | 9.12E-09    | 0      |
| CuHPO4          | 1.64E-10    | 0      |
| Fe(st)OCu (+1)  | 4.21E-09    | 0      |
| *Fe(wk)OCu (+1) | 0.000000288 | 10.3   |
| CuCl3 - (-1)    | 4.11E-19    | 0      |
| CuCl2 AQ        | 1.41E-13    | 0      |
| CuCl -2 1 (-2)  | 1.3E-24     | 0      |
| CuCl + (+1)     | 3.96E-10    | 0      |
| CuCO3 AQ        | 0.000000123 | 4.4    |
| Cu(CO3)2-2 (-2) | 3.51E-11    | 0      |
| CuSO4 AQ        | 8.01E-09    | 0      |
| ATACAMITE       | 0.0276      | *****  |
| AZURITE         | 0.0135      | *****  |
| MALACHITE       | 0.734       | *****  |
| TENORITE        | 5           | *****  |
| CU(OH)2         | 0.477       | *****  |
| CUPRICFERIT     | 0.0191      | *****  |
| CU2(OH)3NO3     | 0.00000368  | *****  |
| ANTLERITE       | 0.00198     | *****  |
| CUOCUSO4        | 5.89E-14    | *****  |
| BROCHANTITE     | 0.018       | *****  |
| LANGITE         | 0.00408     | *****  |
| CU3(PO4)2,3W    | 2.29E-10    | *****  |
| CHALCANTHITE    | 1.51E-08    | *****  |
| MELANOTHALLI    | 1.97E-17    | *****  |
| CUCO3           | 0.0000977   | *****  |
| CU3(PO4)2       | 1.23E-08    | *****  |
| CUSO4           | 8.46E-14    | *****  |

MINEQL output for speciation of copper without considering contribution from sediment

Location 2(Intermediate Period), Ramna Lake

| Name   | Conc.       | %Total |
|--|-------------|--------|
| Cu(2+)   | 0.00000011  | 4      |
| Cu <sub>2</sub> (OH) <sub>2</sub> <sup>2+</sup> (+2) | 2.74E-10    | 0      |
| Cu(OH) <sub>3</sub> <sup>-</sup> (-1)                | 4.39E-12    | 0      |
| Cu(OH) <sub>4</sub> <sup>-2</sup> (-2)               | 3.77E-17    | 0      |
| CuOH <sup>+</sup> (+1)                               | 2.98E-08    | 1.1    |
| Cu(OH) <sub>2</sub> AQ                               | 0.00000197  | 71.9   |
| CuHCO <sub>3</sub> <sup>+</sup> (+1)                 | 6.43E-09    | 0      |
| CuHPO <sub>4</sub>                                   | 1.36E-10    | 0      |
| Fe(st)OCu (+1)                                       | 8.2E-09     | 0      |
| *Fe(wk)OCu (+1)                                      | 0.00000005  | 18.3   |
| CuCl <sub>3</sub> <sup>-</sup> (-1)                  | 2.12E-19    | 0      |
| CuCl <sub>2</sub> AQ                                 | 6.8E-14     | 0      |
| CuCl <sub>4</sub> <sup>-2</sup> 1 (-2)               | 1.41E-24    | 0      |
| CuCl <sup>+</sup> (+1)                               | 1.63E-10    | 0      |
| CuCO <sub>3</sub> AQ                                 | 0.000000109 | 4      |
| Cu(CO <sub>3</sub> ) <sub>2</sub> <sup>-2</sup> (-2) | 4.71E-11    | 0      |
| CuSO <sub>4</sub> AQ                                 | 4.68E-09    | 0      |
| ATACAMITE  | 0.00617     | *****  |
| AZURITE  | 0.00163     | *****  |
| MALACHITE  | 0.185       | *****  |
| TENORITE   | 1.46        | *****  |
| CU(OH) <sub>2</sub>                                  | 0.139       | *****  |
| CUPRICFERIT  | 0.00974     | *****  |
| CU <sub>2</sub> (OH) <sub>3</sub> NO <sub>3</sub>    | 0.000000673 | *****  |
| ANTLERITE  | 0.00108     | *****  |
| CUOCUSO <sub>4</sub>                                 | 2.37E-15    | *****  |
| BROCHANTITE  | 0.0091      | *****  |
| LANGITE  | 0.000103    | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ,3W  | 1.45E-10    | *****  |
| CHALCANTHITE   | 1.08E-08    | *****  |
| MELANOTHALLI   | 8.33E-18    | *****  |
| CUCO <sub>3</sub>                                    | 0.0000867   | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>      | 7.81E-09    | *****  |
| CUSO <sub>4</sub>                                    | 1.38E-14    | *****  |



MINEQL output for speciation of copper without considering contribution from sediment

Location 3(Dry Period), Ramna Lake

| Name            | Conc.       | %Total |
|-----------------|-------------|--------|
| Cu(2+)          | 0.000000646 | 24.8   |
| Cu2(OH)2+2 (+2) | 4.06E-09    | 0      |
| Cu(OH)3 - (-1)  | 8.15E-13    | 0      |
| Cu(OH)4 -2 (-2) | 2.24E-18    | 0      |
| CuOH + (+1)     | 0.000000055 | 2.1    |
| Cu(OH)2 AQ      | 0.00000115  | 44.2   |
| CuHCO3 + (+1)   | 1.24E-08    | 0      |
| CuHPO4          | 1.89E-09    | 0      |
| Fe(st)OCu (+1)  | 2.98E-08    | 1.1    |
| *Fe(wk)OCu (+1) | 0.00000059  | 22.7   |
| CuCl3 - (-1)    | 5.76E-18    | 0      |
| CuCl2 AQ        | 1.24E-12    | 0      |
| CuCl -2 1 (-2)  | 2.7E-23     | 0      |
| CuCl + (+1)     | 2.23E-09    | 0      |
| CuCO3 AQ        | 6.65E-08    | 2.6    |
| Cu(CO3)2-2 (-2) | 3.05E-12    | 0      |
| CuSO4 AQ        | 3.95E-08    | 1.5    |
| ATACAMITE       | 0.036       | *****  |
| AZURITE         | 0.00258     | *****  |
| MALACHITE       | 0.242       | *****  |
| TENORITE        | 3.04        | *****  |
| CU(OH)2         | 0.29        | *****  |
| CUPRICFERIT     | 0.0109      | *****  |
| CU2(OH)3NO3     | 0.00000307  | *****  |
| ANTLERITE       | 0.00281     | *****  |
| CUOCUSO4        | 2.06E-13    | *****  |
| BROCHANTITE     | 0.0138      | *****  |
| LANGITE         | 0.00427     | *****  |
| CU3(PO4)2,3W    | 1.64E-08    | *****  |
| CHALCANTHITE    | 0.00000073  | *****  |
| MELANOTHALLI    | 1.76E-16    | *****  |
| CUCO3           | 0.0000528   | *****  |
| CU3(PO4)2       | 0.00000088  | *****  |
| CUSO4           | 4.77E-13    | *****  |

MINEQL output for speciation of copper without considering contribution from sediment

Location 3(Wet Period), Ramna Lake

| Name  | Conc.       | %Total |
|---|-------------|--------|
| Cu(2+)  | 1.06E-08    | 0      |
| Cu <sub>2</sub> (OH) <sub>2</sub> +2 (+2)           | 9.45E-11    | 0      |
| Cu(OH) <sub>3</sub> - (-1)                          | 1.34E-11    | 0      |
| Cu(OH) <sub>4</sub> -2 (-2)                         | 3.69E-16    | 0      |
| CuOH + (+1)   | 8.98E-09    | 0      |
| Cu(OH) <sub>2</sub> AQ                              | 0.00000188  | 78.2   |
| CuHCO <sub>3</sub> + (+1)                           | 2.01E-09    | 0      |
| CuHPO <sub>4</sub>                                  | 1.6E-12     | 0      |
| Fe(st)OCu (+1)                                      | 2.91E-08    | 1.2    |
| *Fe(wk)OCu (+1)                                     | 0.000000363 | 15.1   |
| CuCl <sub>3</sub> - (-1)                            | 1.89E-20    | 0      |
| CuCl <sub>2</sub> AQ                                | 6.88E-15    | 0      |
| CuCl <sub>4</sub> -2 1 (-2)                         | 5.68E-26    | 0      |
| CuCl + (+1)   | 2.06E-11    | 0      |
| CuCO <sub>3</sub> AQ                                | 0.000000108 | 4.5    |
| Cu(CO <sub>3</sub> ) <sub>2</sub> -2 (-2)           | 4.99E-10    | 0      |
| CuSO <sub>4</sub> AQ                                | 8.29E-10    | 0      |
| ATACAMITE   | 0.00503     | *****  |
| AZURITE   | 0.00922     | *****  |
| MALACHITE   | 0.568       | *****  |
| TENORITE  | 4.4         | *****  |
| CU(OH) <sub>2</sub>                                 | 0.42        | *****  |
| CUPRICFERIT   | 0.0168      | *****  |
| CU <sub>2</sub> (OH) <sub>3</sub> NO <sub>3</sub>   | 0.00000071  | *****  |
| ANTLERITE   | 0.000159    | *****  |
| CUOCUSO <sub>4</sub>                                | 5.37E-15    | *****  |
| BROCHANTITE   | 0.00127     | *****  |
| LANGITE   | 0.000288    | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> .3W | 1.91E-14    | *****  |
| CHALCANTHITE  | 1.56E-09    | *****  |
| MELANOTHALLI  | 9.63E-19    | *****  |
| CUCO <sub>3</sub>                                   | 0.0000859   | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>     | 1.02E-12    | *****  |
| CUSO <sub>4</sub>                                   | 8.76E-15    | *****  |

MINEQL output for speciation of copper without considering contribution from sediment

Location 3(Intermediate Period),Ramna Lake

| Name  | Conc.       | %Total |
|---|-------------|--------|
| Cu(2+)  | 8.95E-08    | 2      |
| Cu <sub>2</sub> (OH) <sub>2</sub> +2 (+2)           | 1.59E-10    | 0      |
| Cu(OH) <sub>3</sub> - (-1)                          | 3.57E-12    | 0      |
| Cu(OH) <sub>4</sub> -2 (-2)                         | 3.99E-17    | 0      |
| CuOH + (+1)   | 2.12E-08    | 0      |
| Cu(OH) <sub>2</sub> AQ                              | 0.0000014   | 31.2   |
| CuHCO <sub>3</sub> + (+1)                           | 4.58E-09    | 0      |
| CuHPO <sub>4</sub>                                  | 2.49E-12    | 0      |
| Fe(st)OCu (+1)                                      | 0.000000206 | 4.6    |
| *Fe(wk)OCu (+1)                                     | 0.00000027  | 59.9   |
| CuCl <sub>3</sub> - (-1)                            | 8.03E-20    | 0      |
| CuCl <sub>2</sub> AQ                                | 2.91E-14    | 0      |
| CuCl <sub>2</sub> -2 1 (-2)                         | 5.4E-25     | 0      |
| CuCl + (+1)   | 8.99E-11    | 0      |
| CuCO <sub>3</sub> AQ                                | 7.77E-08    | 1.7    |
| Cu(CO <sub>3</sub> ) <sub>2</sub> -2 (-2)           | 4.99E-11    | 0      |
| CuSO <sub>4</sub> AQ                                | 1.52E-09    | 0      |
| ATACAMITE   | 0.00243     | *****  |
| AZURITE   | 0.00059     | *****  |
| MALACHITE   | 0.0939      | *****  |
| TENORITE  | 1.04        | *****  |
| CU(OH) <sub>2</sub>                                 | 0.0992      | *****  |
| CUPRICFERIT   | 0.00694     | *****  |
| CU <sub>2</sub> (OH) <sub>3</sub> NO <sub>3</sub>   | 0.000000299 | *****  |
| ANTLERITE   | 0.000178    | *****  |
| CUOCUSO <sub>4</sub>                                | 5.49E-16    | *****  |
| BROCHANTITE   | 0.00107     | *****  |
| LANGITE   | 0.0000121   | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ,3W | 3.47E-14    | *****  |
| CHALCANTHITE  | 3.51E-09    | *****  |
| MELANOTHALLI  | 3.57E-18    | *****  |
| CUCO <sub>3</sub>                                   | 0.0000617   | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>     | 1.86E-12    | *****  |
| CUSO <sub>4</sub>                                   | 4.47E-15    | *****  |

Mineql output for speciation of copper without considering contribution from sediment

Location 4 (Dry Period), Ramna Lake

| Name  | Conc.       | %Total |
|---|-------------|--------|
| Cu(2+)  | 2.59E-10    | 0      |
| Cu <sub>2</sub> (OH) <sub>2</sub> +2 (+2)           | 4E-12       | 0      |
| Cu(OH) <sub>3</sub> - (-1)                          | 1.64E-10    | 0      |
| Cu(OH) <sub>4</sub> -2 (-2)                         | 3.48E-14    | 0      |
| CuOH + (+1)   | 1.78E-09    | 0      |
| Cu(OH) <sub>2</sub> AQ                              | 0.00000295  | 86.8   |
| CuHCO <sub>3</sub> + (+1)                           | 4E-10       | 0      |
| CuHPO <sub>4</sub>                                  | 9.25E-13    | 0      |
| Fe(st)OCu (+1)                                      | 6.04E-09    | 0      |
| *Fe(wk)OCu (+1)                                     | 0.000000223 | 6.6    |
| CuCl <sub>3</sub> - (-1)                            | 1.96E-21    | 0      |
| CuCl <sub>2</sub> AQ                                | 4.52E-16    | 0      |
| CuCl <sub>4</sub> -2 1 (-2)                         | 8.71E-27    | 0      |
| CuCl + (+1)   | 8.48E-13    | 0      |
| CuCO <sub>3</sub> AQ                                | 0.000000171 | 5      |
| Cu(CO <sub>3</sub> ) <sub>2</sub> -2 (-2)           | 4.74E-08    | 1.4    |
| CuSO <sub>4</sub> AQ                                | 1.7E-11     | 0      |
| ATACAMITE   | 0.00273     | *****  |
| AZURITE   | 0.0409      | *****  |
| MALACHITE   | 1.53        | *****  |
| TENORITE  | 7.49        | *****  |
| CU(OH) <sub>2</sub>                                 | 0.716       | *****  |
| CUPRICFERIT   | 0.0275      | *****  |
| CU <sub>2</sub> (OH) <sub>3</sub> NO <sub>3</sub>   | 0.000000246 | *****  |
| ANTLERITE   | 0.00000801  | *****  |
| CUOCUSO <sub>4</sub>                                | 2.08E-16    | *****  |
| BROCHANTITE   | 0.000101    | *****  |
| LANGITE   | 0.0000282   | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ,3W | 1E-14       | *****  |
| CHALCANTHITE  | 3.17E-11    | *****  |
| MELANOTHALLI  | 6.38E-20    | *****  |
| CUCO <sub>3</sub>                                   | 0.000135    | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>     | 5.4E-13     | *****  |
| CUSO <sub>4</sub>                                   | 1.97E-16    | *****  |

Mineql output for speciation of copper without considering contribution from sediment

Location 4 (Wet Period), Ramna Lake

| Name            | Conc.       | %Total |
|-----------------|-------------|--------|
| Cu(2+)          | 8.33E-08    | 4.4    |
| Cu2(OH)2+2 (+2) | 5.61E-10    | 0      |
| Cu(OH)3 - (-1)  | 3.32E-12    | 0      |
| Cu(OH)4 -2 (-2) | 2.88E-17    | 0      |
| CuOH + (+1)     | 2.25E-08    | 1.2    |
| Cu(OH)2 AQ      | 0.00000148  | 78.1   |
| CuHCO3 + (+1)   | 5.03E-09    | 0      |
| CuHPO4          | 5.66E-11    | 0      |
| Fe(st)OCu (+1)  | 2.9E-09     | 0      |
| 'Fe(wk)OCu (+1) | 0.000000211 | 11.1   |
| CuCl3 - (-1)    | 3.53E-19    | 0      |
| CuCl2 AQ        | 9.63E-14    | 0      |
| CuCl -2 1 (-2)  | 1.44E-24    | 0      |
| CuCl + (+1)     | 2.15E-10    | 0      |
| CuCO3 AQ        | 8.54E-08    | 4.5    |
| Cu(CO3)2-2 (-2) | 3.89E-11    | 0      |
| CuSO4 AQ        | 4.38E-09    | 0      |
| ATACAMITE       | 0.0128      | *****  |
| AZURITE         | 0.00426     | *****  |
| MALACHITE       | 0.34        | *****  |
| TENORITE        | 3.34        | *****  |
| CU(OH)2         | 0.319       | *****  |
| CUPRICFERIT     | 0.013       | *****  |
| CU2(OH)3NO3     | 0.00000135  | *****  |
| ANTLERITE       | 0.000526    | *****  |
| CUOCUSO4        | 2.05E-14    | *****  |
| BROCHANTITE     | 0.00333     | *****  |
| LANGITE         | 0.000678    | *****  |
| CU3(PO4)2,3W    | 1.89E-11    | *****  |
| CHALCANTHITE    | 8.33E-09    | *****  |
| MELANOTHALLI    | 1.34E-17    | *****  |
| CUCO3           | 0.0000679   | *****  |
| CU3(PO4)2       | 1.02E-09    | *****  |
| CUSO4           | 4.42E-14    | *****  |



Mineql output for speciation of copper without considering contribution from sediment

Location 4 (Intermediate Period), Ramna Lake

| Name            | Conc.       | %Total |
|-----------------|-------------|--------|
| Cu(2+)          | 0.000000396 | 7.1    |
| Cu2(OH)2+2 (+2) | 2.22E-09    | 0      |
| Cu(OH)3 - (-1)  | 7.92E-12    | 0      |
| Cu(OH)4 -2 (-2) | 5.5E-17     | 0      |
| CuOH + (+1)     | 8.44E-08    | 1.5    |
| Cu(OH)2 AQ      | 0.00000443  | 79.1   |
| CuHCO3 + (+1)   | 1.82E-08    | 0      |
| CuHPO4          | 4.09E-11    | 0      |
| Fe(st)OCu (+1)  | 4.65E-09    | 0      |
| *Fe(wk)OCu (+1) | 0.000000396 | 7.1    |
| CuC3 - (-1)     | 5.13E-19    | 0      |
| CuCl2 AQ        | 1.86E-13    | 0      |
| CuCl4 -2 1 (-2) | 3.05E-24    | 0      |
| CuCl + (+1)     | 5.08E-10    | 0      |
| CuCO3 AQ        | 0.000000245 | 4.4    |
| Cu(CO3)2-2 (-2) | 6.87E-11    | 0      |
| CuSO4 AQ        | 1.84E-08    | 0      |
| ATACAMITE       | 0.0345      | *****  |
| AZURITE         | 0.0186      | *****  |
| MALACHITE       | 0.936       | *****  |
| TENORITE        | 3.28        | *****  |
| CU(OH)2         | 0.313       | *****  |
| CUPRICFERIT     | 0.0219      | *****  |
| CU2(OH)3NO3     | 0.00000425  | *****  |
| ANTLERITE       | 0.0216      | *****  |
| CUOCUSO4        | 2.1E-14     | *****  |
| BROCHANTITE     | 0.408       | *****  |
| LANGITE         | 0.00463     | *****  |
| CU3(PO4)2,3W    | 2.95E-11    | *****  |
| CHALCANTHITE    | 4.25E-08    | *****  |
| MELANOTHALLI    | 2.28E-17    | *****  |
| CUCO3           | 0.000195    | *****  |
| CU3(PO4)2       | 1.58E-09    | *****  |
| CUSO4           | 5.42E-14    | *****  |

# APPENDIX-C

MINEQL output for speciation of copper with considering contribution from sediment

Location 1(Dry Period),Dhanmondi Lake

| Name  | Conc.       | %Total |
|---|-------------|--------|
| Cu(2+)  | 7.38E-08    | 0      |
| Cu <sub>2</sub> (OH) <sub>2</sub> +2 (+2)           | 7.72E-10    | 0      |
| Cu(OH) <sub>3</sub> - (-1)                          | 8.89E-12    | 0      |
| Cu(OH) <sub>4</sub> -2 (-2)                         | 1.14E-16    | 0      |
| CuOH + (+1)   | 2.84E-08    | 0      |
| Cu(OH) <sub>2</sub> AQ                              | 0.00000271  | 4      |
| CuHCO <sub>3</sub> + (+1)                           | 6.32E-09    | 0      |
| CuHPO <sub>4</sub>                                  | 2.6E-12     | 0      |
| Fe(st)OCu (+1)                                      | 0.0000042   | 6.2    |
| *Fe(wk)OCu (+1)                                     | 0.0000608   | 89.4   |
| CuCl <sub>3</sub> - (-1)                            | 1.19E-17    | 0      |
| CuCl <sub>2</sub> AQ                                | 9.38E-13    | 0      |
| CuCl <sub>4</sub> -2 1 (-2)                         | 1.84E-22    | 0      |
| CuCl + (+1)   | 6.08E-10    | 0      |
| CuCO <sub>3</sub> AQ                                | 0.000000155 | 0      |
| Cu(CO <sub>3</sub> ) <sub>2</sub> -2 (-2)           | 1.53E-10    | 0      |
| CuSO <sub>4</sub> AQ                                | 2.92E-09    | 0      |
| ATACAMITE   | 0.0868      | *****  |
| AZURITE   | 0.0206      | *****  |
| MALACHITE   | 0.977       | *****  |
| TENORITE  | 5.29        | *****  |
| CU(OH) <sub>2</sub>                                 | 0.506       | *****  |
| CUPRICFERIT   | 0.0221      | *****  |
| CU <sub>2</sub> (OH) <sub>3</sub> NO <sub>3</sub>   | 0.0000108   | *****  |
| ANTLERITE   | 0.00118     | *****  |
| CUOCUSO <sub>4</sub>                                | 1.82E-14    | *****  |
| BROCHANTITE   | 0.0136      | *****  |
| LANGITE   | 0.00193     | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ,3W | 7.31E-14    | *****  |
| CHALCANTHITE  | 5.69E-09    | *****  |
| MELANOTHALLI  | 1.29E-16    | *****  |
| CUCO <sub>3</sub>                                   | 0.000123    | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>     | 3.92E-12    | *****  |
| CUSO <sub>4</sub>                                   | 2.52E-14    | *****  |

MINEQL output for speciation of copper with considering contribution from sediment

Location 1(Wet Period), Dhanmondi Lake

| Name            | Conc.       | %Total |
|-----------------|-------------|--------|
| Cu(2+)          | 1.18E-09    | 0      |
| Cu2(OH)2+2 (+2) | 3.85E-13    | 0      |
| Cu(OH)3 - (-1)  | 3.74E-13    | 0      |
| Cu(OH)4 -2 (-2) | 6.37E-18    | 0      |
| CuOH + (+1)     | 6.4E-10     | 0      |
| Cu(OH)2 AQ      | 8.43E-08    | 2.6    |
| CuHCO3 + (+1)   | 1.43E-10    | 0      |
| CuHPO4          | 4.35E-13    | 0      |
| Fe(st)OCu (+1)  | 0.000000605 | 18.3   |
| *Fe(wk)OCu (+1) | 0.0000026   | 78.9   |
| CuCl3 - (-1)    | 1.39E-20    | 0      |
| CuCl2 AQ        | 2.68E-15    | 0      |
| CuCl -2 1 (-2)  | 8.65E-26    | 0      |
| CuCl + (+1)     | 4.15E-12    | 0      |
| CuCO3 AQ        | 4.83E-09    | 0      |
| Cu(CO3)2-2 (-2) | 8.52E-12    | 0      |
| CuSO4 AQ        | 4.41E-11    | 0      |
| ATACAMITE       | 0.0000255   | *****  |
| AZURITE         | 0.000000623 | *****  |
| MALACHITE       | 0.000948    | *****  |
| TENORITE        | 0.165       | *****  |
| CU(OH)2         | 0.0157      | *****  |
| CUPRICFERIT     | 0.000687    | *****  |
| CU2(OH)3NO3     | 7.65E-09    | *****  |
| ANTLERITE       | 1.73E-08    | *****  |
| CUOCUSO4        | 8.55E-18    | *****  |
| BROCHANTITE     | 6.23E-09    | *****  |
| LANGITE         | 8.81E-10    | *****  |
| CU3(PO4)2,3W    | 6.34E-17    | *****  |
| CHALCANTHITE    | 8.6E-11     | *****  |
| MELANOTHALLI    | 3.67E-19    | *****  |
| CUCO3           | 0.00000384  | *****  |
| CU3(PO4)2       | 3.41E-15    | *****  |
| CUSO4           | 3.81E-16    | *****  |

MINEQL output for speciation of copper with considering contribution from sediment

Location 1(Intermediate Period), Dhanmondi Lake

| Name  | Conc.       | %Total |
|---|-------------|--------|
| Cu(2+)  | 1.47E-09    | 0      |
| Cu <sub>2</sub> (OH) <sub>2</sub> +2 (+2)           | 2.05E-13    | 0      |
| Cu(OH) <sub>3</sub> - (-1)                          | 4.67E-13    | 0      |
| Cu(OH) <sub>4</sub> -2 (-2)                         | 8.05E-18    | 0      |
| CuOH + (+1)   | 7.94E-10    | 0      |
| Cu(OH) <sub>2</sub> AQ                              | 0.000000105 | 3.6    |
| CuHCO <sub>3</sub> + (+1)                           | 1.71E-10    | 0      |
| CuHPO <sub>4</sub>                                  | 7.33E-13    | 0      |
| Fe(st)OCu (+1)                                      | 0.000000461 | 15.9   |
| *Fe(wk)OCu (+1)                                     | 0.00000233  | 80.2   |
| CuCl <sub>3</sub> - (-1)                            | 1.11E-20    | 0      |
| CuCl <sub>2</sub> AQ                                | 2.27E-15    | 0      |
| CuCl <sub>4</sub> -2 1 (-2)                         | 1.14E-25    | 0      |
| CuCl + (+1)   | 3.47E-12    | 0      |
| CuCO <sub>3</sub> AQ                                | 5.81E-09    | 0      |
| Cu(CO <sub>3</sub> ) <sub>2</sub> -2 (-2)           | 1.01E-11    | 0      |
| CuSO <sub>4</sub> AQ                                | 6.39E-11    | 0      |
| ATACAMITE   | 0.0000144   | *****  |
| AZURITE   | 0.000000264 | *****  |
| MALACHITE   | 0.000548    | *****  |
| TENORITE  | 0.0811      | *****  |
| CU(OH) <sub>2</sub>                                 | 0.00774     | *****  |
| CUPRICFERIT   | 0.000529    | *****  |
| CU <sub>2</sub> (OH) <sub>3</sub> NO <sub>3</sub>   | 4.08E-09    | *****  |
| ANTLERITE   | 4.16E-08    | *****  |
| CUOCUSO <sub>4</sub>                                | 1.9E-18     | *****  |
| BROCHANTITE   | 1.86E-08    | *****  |
| LANGITE   | 2.37E-10    | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ,3W | 2.24E-16    | *****  |
| CHALCANTHITE  | 1.46E-10    | *****  |
| MELANOTHALLI  | 2.79E-19    | *****  |
| CUCO <sub>3</sub>                                   | 0.00000461  | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>     | 1.2E-14     | *****  |
| CUSO <sub>4</sub>                                   | 1.97E-16    | *****  |



MINEQL output for speciation of copper with considering contribution from sediment

Location 2(Dry Period), Dhanmondi Lake

| Name  | Conc.       | %Total |
|---|-------------|--------|
| Cu(2+)  | 2.49E-09    | 0      |
| Cu <sub>2</sub> (OH) <sub>2</sub> 2 <sup>+</sup> (+2) | 1.63E-12    | 0      |
| Cu(OH) <sub>3</sub> <sup>-</sup> (-1)                 | 7.89E-13    | 0      |
| Cu(OH) <sub>4</sub> <sup>-2</sup> (-2)                | 1.4E-17     | 0      |
| CuOH <sup>+</sup> (+1)                                | 1.32E-09    | 0      |
| Cu(OH) <sub>2</sub> AQ                                | 0.000000174 | 3.8    |
| CuHCO <sub>3</sub> <sup>+</sup> (+1)                  | 2.94E-10    | 0      |
| CuHPO <sub>4</sub>                                    | 6.15E-13    | 0      |
| Fe(st)OCu (+1)  | 0.000000656 | 14.3   |
| *Fe(wk)OCu (+1)                                       | 0.000000376 | 81.6   |
| CuCl <sub>3</sub> <sup>-</sup> (-1)                   | 2.92E-19    | 0      |
| CuCl <sub>2</sub> AQ                                  | 2.56E-14    | 0      |
| CuCl <sub>4</sub> <sup>-2</sup> 1 (-2)                | 4.15E-24    | 0      |
| CuCl <sup>+</sup> (+1)                                | 1.83E-11    | 0      |
| CuCO <sub>3</sub> AQ                                  | 9.97E-09    | 0      |
| Cu(CO <sub>3</sub> ) <sub>2</sub> -2 (-2)             | 1.87E-11    | 0      |
| CuSO <sub>4</sub> AQ                                  | 9.49E-11    | 0      |
| ATACAMITE   | 0.000229    |        |
| AZURITE   | 0.00000528  |        |
| MALACHITE   | 0.00394     |        |
| TENORITE  | 0.332       |        |
| CU(OH) <sub>2</sub>                                   | 0.0317      |        |
| CUPRICFERIT   | 0.0014      |        |
| CU <sub>2</sub> (OH) <sub>3</sub> NO <sub>3</sub>     | 3.11E-08    |        |
| ANTLERITE   | 0.000000159 |        |
| CUOCUSO <sub>4</sub>                                  | 3.59E-17    |        |
| BROCHANTITE   | 0.000000118 |        |
| LANGITE   | 1.57E-08    |        |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ,3W   | 2.62E-16    |        |
| CHALCANTHITE  | 1.86E-10    |        |
| MELANOTHALLI  | 3.5E-18     |        |
| CUCO <sub>3</sub>                                     | 0.00000792  |        |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>       | 1.41E-14    |        |
| CUSO <sub>4</sub>                                     | 7.98E-16    |        |

MINEQL output for speciation of copper with considering contribution from sediment

Location 2(Wet Period), Dhanmondi Lake

| Name            | Conc.       | %Total |
|-----------------|-------------|--------|
| Cu(2+)          | 9.06E-09    | 0      |
| Cu2(OH)2+2 (+2) | 3.47E-12    | 0      |
| Cu(OH)3 - (-1)  | 1.81E-13    | 0      |
| Cu(OH)4 -2 (-2) | 1.24E-18    | 0      |
| CuOH + (+1)     | 1.94E-09    | 0      |
| Cu(OH)2 AQ      | 0.000000102 | 2.9    |
| CuHCO3 + (+1)   | 4.32E-10    | 0      |
| CuHPO4          | 9.31E-12    | 0      |
| Fe(st)OCu (+1)  | 0.000000465 | 13.3   |
| *Fe(wk)OCu (+1) | 0.00000292  | 83.3   |
| CuCl3 - (-1)    | 1.31E-19    | 0      |
| CuCl2 AQ        | 2.34E-14    | 0      |
| CuCl -2 1 (-2)  | 8.94E-25    | 0      |
| CuCl + (+1)     | 3.37E-11    | 0      |
| CuCO3 AQ        | 5.83E-09    | 0      |
| Cu(CO3)2-2 (-2) | 1.66E-12    | 0      |
| CuSO4 AQ        | 4.08E-10    | 0      |
| ATACAMITE       | 0.0000978   | *****  |
| AZURITE         | 0.00000106  | *****  |
| MALACHITE       | 0.00135     | *****  |
| TENORITE        | 0.194       | *****  |
| CU(OH)2         | 0.0186      | *****  |
| CUPRICFERIT     | 0.00082     | *****  |
| CU2(OH)3NO3     | 2.71E-08    | *****  |
| ANTLERITE       | 0.000000234 | *****  |
| CUOCUSO4        | 9.04E-17    | *****  |
| BROCHANTITE     | 0.000000102 | *****  |
| LANGITE         | 1.35E-08    | *****  |
| CU3(PO4)2,3W    | 3.52E-14    | *****  |
| CHALCANTHITE    | 7.99E-10    | *****  |
| MELANOTHALLI    | 3.19E-18    | *****  |
| CUCO3           | 0.000000463 | *****  |
| CU3(PO4)2       | 1.89E-12    | *****  |
| CUSO4           | 3.43E-15    | *****  |

MINEQL output for speciation of copper with considering contribution from sediment

Location 2(Intermediate Period), Dhanmondi Lake

| Name  | Conc.       | %Total |
|---|-------------|--------|
| Cu(2+)  | 4.08E-08    | 1.2    |
| Cu <sub>2</sub> (OH) <sub>2</sub> +2 (+2)           | 8.49E-12    | 0      |
| Cu(OH) <sub>3</sub> - (-1)                          | 2.05E-13    | 0      |
| Cu(OH) <sub>4</sub> -2 (-2)                         | 8.94E-19    | 0      |
| CuOH + (+1)   | 5.51E-09    | 0      |
| Cu(OH) <sub>2</sub> AQ                              | 0.000000182 | 5.4    |
| CuHCO <sub>3</sub> + (+1)                           | 1.18E-09    | 0      |
| CuHPO <sub>4</sub>                                  | 1.26E-10    | 0      |
| Fe(st)OCu (+1)                                      | 0.000000267 | 7.9    |
| *Fe(wk)OCu (+1)                                     | 0.00000289  | 85     |
| CuC <sub>3</sub> - (-1)                             | 2.99E-19    | 0      |
| CuCl <sub>2</sub> AQ                                | 6.06E-14    | 0      |
| CuCl <sub>4</sub> -2 1 (-2)                         | 3.35E-24    | 0      |
| CuCl + (+1)   | 9.14E-11    | 0      |
| CuCO <sub>3</sub> AQ                                | 1.01E-08    | 0      |
| Cu(CO <sub>3</sub> ) <sub>2</sub> -2 (-2)           | 1.11E-12    | 0      |
| CuSO <sub>4</sub> AQ                                | 2.26E-09    | 0      |
| ATACAMITE   | 0.000152    | *****  |
| AZURITE   | 0.00000112  | *****  |
| MALACHITE   | 0.00144     | *****  |
| TENORITE  | 0.123       | *****  |
| CU(OH) <sub>2</sub>                                 | 0.0118      | *****  |
| CUPRICFERIT   | 0.000861    | *****  |
| CU <sub>2</sub> (OH) <sub>3</sub> NO <sub>3</sub>   | 4.22E-08    | *****  |
| ANTLERITE   | 0.00000452  | *****  |
| CUOCUSO <sub>4</sub>                                | 8.68E-17    | *****  |
| BROCHANTITE   | 0.00000351  | *****  |
| LANGITE   | 3.16E-08    | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ,3W | 1.15E-11    | *****  |
| CHALCANTHITE  | 5.3E-09     | *****  |
| MELANOTHALLI  | 7.35E-18    | *****  |
| CUCO <sub>3</sub>                                   | 0.000008    | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>     | 6.17E-10    | *****  |
| CUSO <sub>4</sub>                                   | 6.02E-15    | *****  |

MINEQL output for speciation of copper with considering contribution from sediment

Location 3(Dry Period), Dhanmondi Lake

| Name            | Conc.       | %Total |
|-----------------|-------------|--------|
| Cu(2+)          | 4.14E-09    | 0      |
| Cu2(OH)2+2 (+2) | 2.97E-12    | 0      |
| Cu(OH)3 - (-1)  | 6.57E-13    | 0      |
| Cu(OH)4 -2 (-2) | 8.78E-18    | 0      |
| CuOH + (+1)     | 1.79E-09    | 0      |
| Cu(OH)2 AQ      | 0.000000188 | 4.7    |
| CuHCO3 + (+1)   | 3.99E-10    | 0      |
| CuHPO4          | 3.32E-11    | 0      |
| Fe(st)OCu (+1)  | 0.000000393 | 9.8    |
| *Fe(wk)OCu (+1) | 0.00000034  | 85.1   |
| CuCl3 - (-1)    | 5.41E-19    | 0      |
| CuCl2 AQ        | 4.7E-14     | 0      |
| CuCl4 -2 1 (-2) | 7.45E-24    | 0      |
| CuCl + (+1)     | 3.26E-11    | 0      |
| CuCO3 AQ        | 1.07E-08    | 0      |
| Cu(CO3)2-2 (-2) | 1.17E-11    | 0      |
| CuSO4 AQ        | 1.99E-10    | 0      |
| ATACAMITE       | 0.000352    | *****  |
| AZURITE         | 0.00000678  | *****  |
| MALACHITE       | 0.00465     | *****  |
| TENORITE        | 0.364       | *****  |
| CU(OH)2         | 0.0348      | *****  |
| CUPRICFERIT     | 0.00152     | *****  |
| CU2(OH)3NO3     | 4.76E-08    | *****  |
| ANTLERITE       | 0.000000387 | *****  |
| CUOCUSO4        | 8.42E-17    | *****  |
| BROCHANTITE     | 0.00000031  | *****  |
| LANGITE         | 4.29E-08    | *****  |
| CU3(PO4)2,3W    | 8.23E-13    | *****  |
| CHALCANTHITE    | 3.89E-10    | *****  |
| MELANOTHALLI    | 6.44E-18    | *****  |
| CUCO3           | 0.00000854  | *****  |
| CU3(PO4)2       | 4.42E-11    | *****  |
| CUSO4           | 1.71E-15    | *****  |

MINEQL output for speciation of copper with considering contribution from sediment

Location 3(Wet Period), Dhanmondi Lake

| Name  | Conc.       | %Total |
|---|-------------|--------|
| Cu(2+)  | 2.53E-09    | 0      |
| Cu <sub>2</sub> (OH) <sub>2</sub> +2 (+2)           | 4.01E-13    | 0      |
| Cu(OH) <sub>3</sub> - (-1)                          | 1.01E-13    | 0      |
| Cu(OH) <sub>4</sub> -2 (-2)                         | 8.72E-19    | 0      |
| CuOH + (+1)   | 6.83E-10    | 0      |
| Cu(OH) <sub>2</sub> AQ                              | 4.51E-08    | 1.7    |
| CuHCO <sub>3</sub> + (+1)                           | 1.52E-10    | 0      |
| CuHPO <sub>4</sub>                                  | 2.25E-12    | 0      |
| Fe(st)OCu (+1)                                      | 0.000000521 | 20     |
| *Fe(wk)OCu (+1)                                     | 0.00000203  | 78     |
| CuCl <sub>3</sub> - (-1)                            | 2.91E-20    | 0      |
| CuCl <sub>2</sub> AQ                                | 5.58E-15    | 0      |
| CuCl <sub>4</sub> -2 1 (-2)                         | 1.92E-25    | 0      |
| CuCl + (+1)   | 8.58E-12    | 0      |
| CuCO <sub>3</sub> AQ                                | 2.58E-09    | 0      |
| Cu(CO <sub>3</sub> ) <sub>2</sub> -2 (-2)           | 1.16E-12    | 0      |
| CuSO <sub>4</sub> AQ                                | 1.53E-10    | 0      |
| ATACAMITE   | 0.0000134   | *****  |
| AZURITE   | 8.34E-08    | *****  |
| MALACHITE   | 0.000249    | *****  |
| TENORITE  | 0.0812      | *****  |
| CU(OH) <sub>2</sub>                                 | 0.00776     | *****  |
| CUPRICFERIT   | 0.000352    | *****  |
| CU <sub>2</sub> (OH) <sub>3</sub> NO <sub>3</sub>   | 3.95E-09    | *****  |
| ANTLERITE   | 1.73E-08    | *****  |
| CUOCUSO <sub>4</sub>                                | 1.31E-17    | *****  |
| BROCHANTITE   | 3.32E-09    | *****  |
| LANGITE   | 3.79E-10    | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ,3W | 9.13E-16    | *****  |
| CHALCANTHITE  | 3.02E-10    | *****  |
| MELANOTHALLI  | 7.57E-19    | *****  |
| CUCO <sub>3</sub>                                   | 0.00000205  | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>     | 4.9E-14     | *****  |
| CUSO <sub>4</sub>                                   | 1.2E-15     | *****  |



MINEQL output for speciation of copper with considering contribution from sediment

Location 3(Intermediate Period), Dhanmondi Lake

| Name   | Conc.       | %Total |
|--|-------------|--------|
| Cu(2+)   | 1.28E-08    | 0      |
| Cu <sub>2</sub> (OH) <sub>2</sub> <sup>2+</sup> (+2) | 1.38E-12    | 0      |
| Cu(OH) <sub>3</sub> <sup>-</sup> (-1)                | 1.28E-13    | 0      |
| Cu(OH) <sub>4</sub> <sup>-2</sup> (-2)               | 7.01E-19    | 0      |
| CuOH <sup>+</sup> (+1)                               | 2.16E-09    | 0      |
| Cu(OH) <sub>2</sub> AQ                               | 9.02E-08    | 3      |
| CuHCO <sub>3</sub> <sup>+</sup> (+1)                 | 4.66E-10    | 0      |
| CuHPO <sub>4</sub>                                   | 3.11E-11    | 0      |
| Fe(st)OCu (+1)                                       | 0.000000351 | 11.7   |
| *Fe(wk)OCu (+1)                                      | 0.00000254  | 84.6   |
| CuCl <sub>3</sub> <sup>-</sup> (-1)                  | 1.15E-19    | 0      |
| CuCl <sub>2</sub> AQ                                 | 2.18E-14    | 0      |
| CuCl <sub>4</sub> <sup>-2</sup> (-2)                 | 1.34E-24    | 0      |
| CuCl <sup>+</sup> (+1)                               | 3.1E-11     | 0      |
| CuCO <sub>3</sub> AQ                                 | 4.99E-09    | 0      |
| Cu(CO <sub>3</sub> ) <sub>2</sub> <sup>-2</sup> (-2) | 8.74E-13    | 0      |
| CuSO <sub>4</sub> AQ                                 | 7.92E-10    | 0      |
| ATACAMITE  | 0.000033    | *****  |
| AZURITE  | 0.000000146 | *****  |
| MALACHITE  | 0.00037     | *****  |
| TENORITE   | 0.0639      | *****  |
| CU(OH) <sub>2</sub>                                  | 0.0061      | *****  |
| CUPRICFERIT  | 0.000436    | *****  |
| CU <sub>2</sub> (OH) <sub>3</sub> NO <sub>3</sub>    | 8.63E-09    | *****  |
| ANTLERITE  | 0.000000386 | *****  |
| CUOCUSO <sub>4</sub>                                 | 1.66E-17    | *****  |
| BROCHANTITE  | 0.000000148 | *****  |
| LANGITE  | 1.5E-09     | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ·3W  | 3.46E-13    | *****  |
| CHALCANTHITE   | 1.84E-09    | *****  |
| MELANOTHALLI   | 2.66E-18    | *****  |
| CUCO <sub>3</sub>                                    | 0.00000396  | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>      | 1.86E-11    | *****  |
| CUSO <sub>4</sub>                                    | 2.22E-15    | *****  |

MINEQL output for speciation of copper with considering contribution from sediment

Location 4(Dry Period), Dhanmondi Lake

| Name  | Conc.       | %Total |
|---|-------------|--------|
| Cu(2+)  | 2.72E-09    | 0      |
| Cu <sub>2</sub> (OH) <sub>2</sub> +2 (+2)           | 1.21E-12    | 0      |
| Cu(OH) <sub>3</sub> - (-1)                          | 4.32E-13    | 0      |
| Cu(OH) <sub>4</sub> -2 (-2)                         | 6.16E-18    | 0      |
| CuOH + (+1)   | 1.14E-09    | 0      |
| Cu(OH) <sub>2</sub> AQ                              | 0.000000119 | 3.3    |
| CuHCO <sub>3</sub> + (+1)                           | 2.54E-10    | 0      |
| CuHPO <sub>4</sub>                                  | 8.89E-13    | 0      |
| Fe(st)OCu (+1)                                      | 0.000000556 | 15.5   |
| *Fe(wk)OCu (+1)                                     | 0.00000291  | 80.9   |
| CuCl <sub>3</sub> - (-1)                            | 2.52E-19    | 0      |
| CuCl <sub>2</sub> AQ                                | 2.37E-14    | 0      |
| CuCl <sub>2</sub> -2 1 (-2)                         | 3.36E-24    | 0      |
| CuCl + (+1)   | 1.84E-11    | 0      |
| CuCO <sub>3</sub> AQ                                | 6.84E-09    | 0      |
| Cu(CO <sub>3</sub> ) <sub>2</sub> -2 (-2)           | 8.21E-12    | 0      |
| CuSO <sub>4</sub> AQ                                | 1.82E-10    | 0      |
| ATACAMITE   | 0.000124    | *****  |
| AZURITE   | 0.00000168  | *****  |
| MALACHITE   | 0.00184     | *****  |
| TENORITE  | 0.226       | *****  |
| CU(OH) <sub>2</sub>                                 | 0.0216      | *****  |
| CUPRICFERIT   | 0.000957    | *****  |
| CU <sub>2</sub> (OH) <sub>3</sub> NO <sub>3</sub>   | 1.83E-08    | *****  |
| ANTLERITE   | 0.000000143 | *****  |
| CUOCUSO <sub>4</sub>                                | 4.62E-17    | *****  |
| BROCHANTITE   | 0.000000073 | *****  |
| LANGITE   | 9.48E-09    | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> .3W | 3.76E-16    | *****  |
| CHALCANTHITE  | 3.56E-10    | *****  |
| MELANOTHALLI  | 3.24E-18    | *****  |
| CUCO <sub>3</sub>                                   | 0.00000543  | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>     | 2.02E-14    | *****  |
| CUSO <sub>4</sub>                                   | 1.51E-15    | *****  |

MINEQL output for speciation of copper with considering contribution from sediment

Location 4(Wet Period), Dhanmondi Lake

| Name   | Conc.       | %Total |
|--|-------------|--------|
| Cu(2+)   | 2.94E-09    | 0      |
| Cu <sub>2</sub> (OH) <sub>2</sub> <sup>2+</sup> (+2) | 3.15E-13    | 0      |
| Cu(OH) <sub>3</sub> <sup>-</sup> (-1)                | 5.88E-14    | 0      |
| Cu(OH) <sub>4</sub> <sup>-2</sup> (-2)               | 4.08E-19    | 0      |
| CuOH <sup>+</sup> (+1)                               | 6.27E-10    | 0      |
| Cu(OH) <sub>2</sub> AQ                               | 3.29E-08    | 1.1    |
| CuHCO <sub>3</sub> <sup>+</sup> (+1)                 | 1.39E-10    | 0      |
| CuHPO <sub>4</sub>                                   | 1.92E-12    | 0      |
| Fe(st)OCu (+1)                                       | 0.000000672 | 23.2   |
| *Fe(wk)OCu (+1)                                      | 0.00000219  | 75.5   |
| CuCl <sub>3</sub> <sup>-</sup> (-1)                  | 2.42E-20    | 0      |
| CuCl <sub>2</sub> AQ                                 | 5.13E-15    | 0      |
| CuCl <sub>4</sub> <sup>-2</sup> 1 (-2)               | 1.52E-25    | 0      |
| CuCl <sup>+</sup> (+1)                               | 8.72E-12    | 0      |
| CuCO <sub>3</sub> AQ                                 | 1.88E-09    | 0      |
| Cu(CO <sub>3</sub> ) <sub>2</sub> <sup>-2</sup> (-2) | 5.4E-13     | 0      |
| CuSO <sub>4</sub> AQ                                 | 1.7E-10     | 0      |
| ATACAMITE  | 0.00000753  | *****  |
| AZURITE  | 0.000000029 | *****  |
| MALACHITE  | 0.000123    | *****  |
| TENORITE   | 0.0554      | *****  |
| CU(OH) <sub>2</sub>                                  | 0.00529     | *****  |
| CUPRICFERIT  | 0.000248    | *****  |
| CU <sub>2</sub> (OH) <sub>3</sub> NO <sub>3</sub>    | 2.44E-09    | *****  |
| ANTLERITE  | 1.02E-08    | *****  |
| CUOCUSO <sub>4</sub>                                 | 9.14E-18    | *****  |
| BROCHANTITE  | 1.44E-09    | *****  |
| LANGITE  | 1.38E-10    | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> .3W  | 4.83E-16    | *****  |
| CHALCANTHITE   | 3.39E-10    | *****  |
| MELANOTHALLI   | 6.9E-19     | *****  |
| CUCO <sub>3</sub>                                    | 0.00000149  | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>      | 2.59E-14    | *****  |
| CUSO <sub>4</sub>                                    | 1.24E-15    | *****  |

MINEQL output for speciation of copper with considering contribution from sediment

Location 4(Intermediate Period), Dhanmondi Lake

| Name  | Conc.       | %Total |
|---|-------------|--------|
| Cu(2+)  | 2.71E-11    | 0      |
| Cu <sub>2</sub> (OH) <sub>2</sub> +2 (+2)           | 4.43E-15    | 0      |
| Cu(OH) <sub>3</sub> - (-1)                          | 4.31E-12    | 0      |
| Cu(OH) <sub>4</sub> -2 (-2)                         | 5.78E-16    | 0      |
| CuOH + (+1)   | 1.17E-10    | 0      |
| Cu(OH) <sub>2</sub> AQ                              | 0.000000123 | 5.1    |
| CuHCO <sub>3</sub> + (+1)                           | 2.53E-11    | 0      |
| CuHPO <sub>4</sub>                                  | 3.42E-13    | 0      |
| Fe(st)OCu (+1)                                      | 0.000000394 | 16.4   |
| *Fe(wk)OCu (+1)                                     | 0.00000188  | 78.1   |
| CuCl <sub>3</sub> - (-1)                            | 3.53E-22    | 0      |
| CuCl <sub>2</sub> AQ                                | 6.06E-17    | 0      |
| CuCl <sub>4</sub> -2 1 (-2)                         | 4.25E-27    | 0      |
| CuCl + (+1)   | 7.72E-14    | 0      |
| CuCO <sub>3</sub> AQ                                | 6.81E-09    | 0      |
| Cu(CO <sub>3</sub> ) <sub>2</sub> -2 (-2)           | 7.25E-10    | 0      |
| CuSO <sub>4</sub> AQ                                | 1.84E-12    | 0      |
| ATACAMITE   | 0.00000298  | *****  |
| AZURITE   | 0.000000425 | *****  |
| MALACHITE   | 0.000753    | *****  |
| TENORITE  | 0.095       | *****  |
| CU(OH) <sub>2</sub>                                 | 0.00907     | *****  |
| CUPRICFERIT   | 0.000621    | *****  |
| CU <sub>2</sub> (OH) <sub>3</sub> NO <sub>3</sub>   | 7.13E-10    | *****  |
| ANTLERITE   | 1.65E-09    | *****  |
| CUOCUSO <sub>4</sub>                                | 6.44E-20    | *****  |
| BROCHANTITE   | 8.64E-10    | *****  |
| LANGITE   | 1.1E-11     | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ,3W | 5.7E-17     | *****  |
| CHALCANTHITE  | 4.22E-12    | *****  |
| MELANOTHALLI  | 7.46E-21    | *****  |
| CUCO <sub>3</sub>                                   | 0.00000541  | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>     | 3.06E-15    | *****  |
| CUSO <sub>4</sub>                                   | 5.7E-18     | *****  |

MINEQL output for speciation of copper with considering contribution from sediment

Location 5(Dry Peeriod), Dhanmondi Lake

| Name  | Conc.       | %Total |
|---|-------------|--------|
| Cu(2+)  | 2.22E-09    | 0      |
| Cu <sub>2</sub> (OH) <sub>2</sub> +2 (+2)           | 1.99E-12    | 0      |
| Cu(OH) <sub>3</sub> - (-1)                          | 1.22E-12    | 0      |
| Cu(OH) <sub>4</sub> -2 (-2)                         | 2.59E-17    | 0      |
| CuOH + (+1)   | 1.42E-09    | 0      |
| Cu(OH) <sub>2</sub> AQ                              | 0.000000225 | 5.8    |
| CuHCO <sub>3</sub> + (+1)                           | 3.17E-10    | 0      |
| CuHPO <sub>4</sub>                                  | 5.28E-13    | 0      |
| Fe(st)OCu (+1)                                      | 0.000000505 | 13     |
| *Fe(wk)OCu (+1)                                     | 0.00000315  | 80.8   |
| CuCl <sub>3</sub> - (-1)                            | 1.5E-19     | 0      |
| CuCl <sub>2</sub> AQ                                | 1.6E-14     | 0      |
| CuCl <sub>4</sub> -2 1 (-2)                         | 1.7E-24     | 0      |
| CuCl + (+1)   | 1.38E-11    | 0      |
| CuCO <sub>3</sub> AQ                                | 1.29E-08    | 0      |
| Cu(CO <sub>3</sub> ) <sub>2</sub> -2 (-2)           | 3.47E-11    | 0      |
| CuSO <sub>4</sub> AQ                                | 1.3E-10     | 0      |
| ATACAMITE   | 0.000278    | *****  |
| AZURITE   | 0.0000124   | *****  |
| MALACHITE   | 0.00694     | *****  |
| TENORITE  | 0.451       | *****  |
| CU(OH) <sub>2</sub>                                 | 0.0431      | *****  |
| CUPRICFERIT   | 0.00186     | *****  |
| CU <sub>2</sub> (OH) <sub>3</sub> NO <sub>3</sub>   | 4.59E-08    | *****  |
| ANTLERITE   | 0.000000363 | *****  |
| CUOCUSO <sub>4</sub>                                | 7.1E-17     | *****  |
| BROCHANTITE   | 0.000000348 | *****  |
| LANGITE   | 5.26E-08    | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ,3W | 2.5E-16     | *****  |
| CHALCANTHITE  | 2.52E-10    | *****  |
| MELANOTHALLI  | 2.19E-18    | *****  |
| CUCO <sub>3</sub>                                   | 0.0000103   | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>     | 1.34E-14    | *****  |
| CUSO <sub>4</sub>                                   | 1.15E-15    | *****  |



MINEQL output for speciation of copper with considering contribution from sediment

Location 5(Wet Period), Dhanmondi Lake

| Name   | Conc.       | %Total |
|--|-------------|--------|
| Cu(2+)   | 3.14E-10    | 0      |
| Cu <sub>2</sub> (OH) <sub>2</sub> <sup>2+</sup> (+2) | 6.24E-14    | 0      |
| Cu(OH) <sub>3</sub> <sup>-</sup> (-1)                | 3.96E-13    | 0      |
| Cu(OH) <sub>4</sub> <sup>-2</sup> (-2)               | 1.1E-17     | 0      |
| CuOH <sup>+</sup> (+1)                               | 2.66E-10    | 0      |
| Cu(OH) <sub>2</sub> AQ                               | 5.55E-08    | 1.7    |
| CuHCO <sub>3</sub> <sup>+</sup> (+1)                 | 5.91E-11    | 0      |
| CuHPO <sub>4</sub>                                   | 4.19E-14    | 0      |
| Fe(st)OCu (+1)                                       | 0.000000564 | 17.6   |
| *Fe(wk)OCu (+1)                                      | 0.00000258  | 80.5   |
| CuCl <sub>3</sub> <sup>-</sup> (-1)                  | 2.82E-21    | 0      |
| CuCl <sub>2</sub> AQ                                 | 5.83E-16    | 0      |
| CuCl <sub>4</sub> <sup>-2</sup> (-2)                 | 1.73E-26    | 0      |
| CuCl <sup>+</sup> (+1)                               | 9.76E-13    | 0      |
| CuCO <sub>3</sub> AQ                                 | 3.17E-09    | 0      |
| Cu(CO <sub>3</sub> ) <sub>2</sub> <sup>-2</sup> (-2) | 1.47E-11    | 0      |
| CuSO <sub>4</sub> AQ                                 | 1.51E-11    | 0      |
| ATACAMITE  | 0.00000599  | *****  |
| AZURITE  | 0.000000159 | *****  |
| MALACHITE  | 0.000383    | *****  |
| TENORITE   | 0.102       | *****  |
| CU(OH) <sub>2</sub>                                  | 0.0097      | *****  |
| CUPRICFERIT  | 0.000437    | *****  |
| CU <sub>2</sub> (OH) <sub>3</sub> NO <sub>3</sub>    | 1.91E-09    | *****  |
| ANTLERITE  | 2.57E-09    | *****  |
| CUOCUSO <sub>4</sub>                                 | 1.65E-18    | *****  |
| BROCHANTITE  | 6.09E-10    | *****  |
| LANGITE  | 7.25E-11    | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ,3W  | 3.89E-19    | *****  |
| CHALCANTHITE   | 2.97E-11    | *****  |
| MELANOTHALLI   | 7.93E-20    | *****  |
| CUCO <sub>3</sub>                                    | 0.00000252  | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>      | 2.09E-17    | *****  |
| CUSO <sub>4</sub>                                    | 1.21E-16    | *****  |

MINEQL output for speciation of copper with considering contribution from sediment

Location 5(Intermediate Period), Dhanmondi Lake

| Name  | Conc.       | %Total |
|---|-------------|--------|
| Cu(2+)  | 2.22E-10    | 0      |
| Cu <sub>2</sub> (OH) <sub>2</sub> +2 (+2)           | 1.65E-14    | 0      |
| Cu(OH) <sub>3</sub> - (-1)                          | 5.58E-13    | 0      |
| Cu(OH) <sub>4</sub> -2 (-2)                         | 1.95E-17    | 0      |
| CuOH + (+1)   | 2.36E-10    | 0      |
| Cu(OH) <sub>2</sub> AQ                              | 6.21E-08    | 3.1    |
| CuHCO <sub>3</sub> + (+1)                           | 5.08E-11    | 0      |
| CuHPO <sub>4</sub>                                  | 4.16E-14    | 0      |
| Fe(st)OCu (+1)                                      | 0.000000313 | 15.6   |
| *Fe(wk)OCu (+1)                                     | 0.00000162  | 81.1   |
| CuCl <sub>3</sub> - (-1)                            | 1.97E-21    | 0      |
| CuCl <sub>2</sub> AQ                                | 3.74E-16    | 0      |
| CuCl <sub>4</sub> -2 1 (-2)                         | 2.31E-26    | 0      |
| CuCl + (+1)   | 5.32E-13    | 0      |
| CuCO <sub>3</sub> AQ                                | 3.43E-09    | 0      |
| Cu(CO <sub>3</sub> ) <sub>2</sub> -2 (-2)           | 2.43E-11    | 0      |
| CuSO <sub>4</sub> AQ                                | 1.15E-11    | 0      |
| ATACAMITE   | 0.00000246  | *****  |
| AZURITE   | 4.75E-08    | *****  |
| MALACHITE   | 0.000175    | *****  |
| TENORITE  | 0.044       | *****  |
| CU(OH) <sub>2</sub>                                 | 0.0042      | *****  |
| CUPRICFERIT   | 0.0003      | *****  |
| CU <sub>2</sub> (OH) <sub>3</sub> NO <sub>3</sub>   | 6.44E-10    | *****  |
| ANTLERITE   | 2.65E-09    | *****  |
| CUOCUSO <sub>4</sub>                                | 1.66E-19    | *****  |
| BROCHANTITE   | 7E-10       | *****  |
| LANGITE   | 7.08E-12    | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ,3W | 4.28E-19    | *****  |
| CHALCANTHITE  | 2.67E-11    | *****  |
| MELANOTHALLI  | 4.55E-20    | *****  |
| CUCO <sub>3</sub>                                   | 0.00000273  | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>     | 2.3E-17     | *****  |
| CUSO <sub>4</sub>                                   | 3.21E-17    | *****  |

MINEQL output for speciation of copper with considering contribution from sediment

Location 6(Dry Period), Dhanmondi Lake

| Name  | Conc.       | %Total |
|---|-------------|--------|
| Cu(2+)  | 2.72E-09    | 0      |
| Cu <sub>2</sub> (OH) <sub>2</sub> +2 (+2)           | 1.97E-12    | 0      |
| Cu(OH) <sub>3</sub> - (-1)                          | 8.62E-13    | 0      |
| Cu(OH) <sub>4</sub> -2 (-2)                         | 1.55E-17    | 0      |
| CuOH + (+1)   | 1.44E-09    | 0      |
| Cu(OH) <sub>2</sub> AQ                              | 0.000000189 | 5.3    |
| CuHCO <sub>3</sub> + (+1)                           | 3.2E-10     | 0      |
| CuHPO <sub>4</sub>                                  | 6.16E-13    | 0      |
| Fe(st)OCu (+1)                                      | 0.000000489 | 13.6   |
| *Fe(wk)OCu (+1)                                     | 0.00000291  | 80.7   |
| CuCl <sub>3</sub> - (-1)                            | 4.28E-19    | 0      |
| CuCl <sub>2</sub> AQ                                | 3.39E-14    | 0      |
| CuCl <sub>4</sub> -2 1 (-2)                         | 6.7E-24     | 0      |
| CuCl + (+1)   | 2.21E-11    | 0      |
| CuCO <sub>3</sub> AQ                                | 1.08E-08    | 0      |
| Cu(CO <sub>3</sub> ) <sub>2</sub> -2 (-2)           | 2.07E-11    | 0      |
| CuSO <sub>4</sub> AQ                                | 1.25E-10    | 0      |
| ATACAMITE   | 0.000302    | *****  |
| AZURITE   | 0.00000694  | *****  |
| MALACHITE   | 0.00473     | *****  |
| TENORITE  | 0.367       | *****  |
| CU(OH) <sub>2</sub>                                 | 0.035       | *****  |
| CUPRICFERIT   | 0.00153     | *****  |
| CU <sub>2</sub> (OH) <sub>3</sub> NO <sub>3</sub>   | 3.71E-08    | *****  |
| ANTLERITE   | 0.000000246 | *****  |
| CUOCUSO <sub>4</sub>                                | 5.32E-17    | *****  |
| BROCHANTITE   | 0.000000199 | *****  |
| LANGITE   | 2.75E-08    | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ,3W | 2.86E-16    | *****  |
| CHALCANTHITE  | 2.43E-10    | *****  |
| MELANOTHALLI  | 4.63E-18    | *****  |
| CUCO <sub>3</sub>                                   | 0.00000861  | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>     | 1.53E-14    | *****  |
| CUSO <sub>4</sub>                                   | 1.07E-15    | *****  |

MINEQL output for speciation of copper with considering contribution from sediment

Location 6(Wet Period), Dhanmondi Lake

| Name  | Conc.       | %Total |
|---|-------------|--------|
| Cu(2+)  | 2.16E-09    | 0      |
| Cu <sub>2</sub> (OH) <sub>2</sub> +2 (+2)           | 4.7E-13     | 0      |
| Cu(OH) <sub>3</sub> - (-1)                          | 1.72E-13    | 0      |
| Cu(OH) <sub>4</sub> -2 (-2)                         | 1.87E-18    | 0      |
| CuOH + (+1)   | 7.32E-10    | 0      |
| Cu(OH) <sub>2</sub> AQ                              | 6.09E-08    | 1.9    |
| CuHCO <sub>3</sub> + (+1)                           | 1.63E-10    | 0      |
| CuHPO <sub>4</sub>                                  | 1.71E-12    | 0      |
| Fe(st)OCu (+1)                                      | 0.000000599 | 18.7   |
| *Fe(wk)OCu (+1)                                     | 0.00000253  | 79.2   |
| CuCl <sub>3</sub> - (-1)                            | 2.86E-20    | 0      |
| CuCl <sub>2</sub> AQ                                | 5.23E-15    | 0      |
| CuCl <sub>4</sub> -2 1 (-2)                         | 1.96E-25    | 0      |
| CuCl + (+1)   | 7.7E-12     | 0      |
| CuCO <sub>3</sub> AQ                                | 3.48E-09    | 0      |
| Cu(CO <sub>3</sub> ) <sub>2</sub> -2 (-2)           | 2.49E-12    | 0      |
| CuSO <sub>4</sub> AQ                                | 1.52E-10    | 0      |
| ATACAMITE   | 0.0000206   | *****  |
| AZURITE   | 0.00000021  | *****  |
| MALACHITE   | 0.00046     | *****  |
| TENORITE  | 0.111       | *****  |
| CU(OH) <sub>2</sub>                                 | 0.0106      | *****  |
| CUPRICFERIT   | 0.000479    | *****  |
| CU <sub>2</sub> (OH) <sub>3</sub> NO <sub>3</sub>   | 5.82E-09    | *****  |
| ANTLERITE   | 3.12E-08    | *****  |
| CUOCUSO <sub>4</sub>                                | 1.83E-17    | *****  |
| BROCHANTITE   | 8.09E-09    | *****  |
| LANGITE   | 9.64E-10    | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ,3W | 7.09E-16    | *****  |
| CHALCANTHITE  | 2.99E-10    | *****  |
| MELANOTHALLI  | 7.11E-19    | *****  |
| CUCO <sub>3</sub>                                   | 0.00000276  | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>     | 3.81E-14    | *****  |
| CUSO <sub>4</sub>                                   | 1.22E-15    | *****  |

MINEQL output for speciation of copper with considering contribution from sediment

Location 6(Intermediate Period), Dhanmondi Lake

| Name            | Conc.       | %Total |
|-----------------|-------------|--------|
| Cu(2+)          | 1.11E-08    | 0      |
| Cu2(OH)2+2 (+2) | 1.11E-12    | 0      |
| Cu(OH)3 - (-1)  | 1.12E-13    | 0      |
| Cu(OH)4 -2 (-2) | 6.15E-19    | 0      |
| CuOH + (+1)     | 1.89E-09    | 0      |
| Cu(OH)2 AQ      | 7.88E-08    | 3.4    |
| CuHCO3 + (+1)   | 4.07E-10    | 0      |
| CuHPO4          | 2.63E-11    | 0      |
| Fe(st)OCu (+1)  | 0.000000285 | 12.4   |
| *Fe(wk)OCu (+1) | 0.00000192  | 83.4   |
| CuCl3 - (-1)    | 1.14E-19    | 0      |
| CuCl2 AQ        | 2.08E-14    | 0      |
| CuCl -2 1 (-2)  | 1.35E-24    | 0      |
| CuCl + (+1)     | 2.85E-11    | 0      |
| CuCO3 AQ        | 4.36E-09    | 0      |
| Cu(CO3)2-2 (-2) | 7.68E-13    | 0      |
| CuSO4 AQ        | 6.91E-10    | 0      |
| ATACAMITE       | 0.0000273   | *****  |
| AZURITE         | 0.000000104 | *****  |
| MALACHITE       | 0.000296    | *****  |
| TENORITE        | 0.0583      | *****  |
| CU(OH)2         | 0.00557     | *****  |
| CUPRICFERIT     | 0.000389    | *****  |
| CU2(OH)3NO3     | 6.91E-09    | *****  |
| ANTLERITE       | 0.000000255 | *****  |
| CUOCUSO4        | 1.4E-17     | *****  |
| BROCHANTITE     | 8.58E-08    | *****  |
| LANGITE         | 9.74E-10    | *****  |
| CU3(PO4)2,3W    | 2.17E-13    | *****  |
| CHALCANTHITE    | 1.59E-09    | *****  |
| MELANOTHALLI    | 2.55E-18    | *****  |
| CUCO3           | 0.00000347  | *****  |
| CU3(PO4)2       | 1.17E-11    | *****  |
| CUSO4           | 2.03E-15    | *****  |



MINEQL output for speciation of copper with considering contribution from sediment

Location 7(Dry Period), Dhanmondi Lake

| Name  | Conc.       | %Total |
|---|-------------|--------|
| Cu(2+)  | 1.75E-09    | 0      |
| Cu <sub>2</sub> (OH) <sub>2</sub> +2 (+2)           | 1.58E-12    | 0      |
| Cu(OH) <sub>3</sub> - (-1)                          | 1.46E-12    | 0      |
| Cu(OH) <sub>4</sub> -2 (-2)                         | 3.62E-17    | 0      |
| CuOH + (+1)   | 1.27E-09    | 0      |
| Cu(OH) <sub>2</sub> AQ                              | 0.000000231 | 4.7    |
| CuHCO <sub>3</sub> + (+1)                           | 2.83E-10    | 0      |
| CuHPO <sub>4</sub>                                  | 3.09E-13    | 0      |
| Fe(st)OCu (+1)                                      | 0.000000645 | 13.2   |
| *Fe(wk)OCu (+1)                                     | 0.00000401  | 81.8   |
| CuCl <sub>3</sub> - (-1)                            | 4.81E-19    | 0      |
| CuCl <sub>2</sub> AQ                                | 3.16E-14    | 0      |
| CuCl <sub>4</sub> -2 1 (-2)                         | 9.03E-24    | 0      |
| CuCl + (+1)   | 1.71E-11    | 0      |
| CuCO <sub>3</sub> AQ                                | 1.32E-08    | 0      |
| Cu(CO <sub>3</sub> ) <sub>2</sub> -2 (-2)           | 4.83E-11    | 0      |
| CuSO <sub>4</sub> AQ                                | 8.8E-11     | 0      |
| ATACAMITE   | 0.000397    | *****  |
| AZURITE   | 0.0000128   | *****  |
| MALACHITE   | 0.00713     | *****  |
| TENORITE  | 0.452       | *****  |
| CU(OH) <sub>2</sub>                                 | 0.0432      | *****  |
| CUPRICFERIT   | 0.00188     | *****  |
| CU <sub>2</sub> (OH) <sub>3</sub> NO <sub>3</sub>   | 4.05E-08    | *****  |
| ANTLERITE   | 0.00000028  | *****  |
| CUOCUSO <sub>4</sub>                                | 4.67E-17    | *****  |
| BROCHANTITE   | 0.000000256 | *****  |
| LANGITE   | 3.62E-08    | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ,3W | 8.79E-17    | *****  |
| CHALCANTHITE  | 1.71E-10    | *****  |
| MELANOTHALLI  | 4.32E-18    | *****  |
| CUCO <sub>3</sub>                                   | 0.0000105   | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>     | 4.72E-15    | *****  |
| CUSO <sub>4</sub>                                   | 7.61E-16    | *****  |

MINEQL output for speciation of copper with considering contribution from sediment

Location 7(Wet Period), Dhanmondi Lake

| Name  | Conc.       | %Total |
|---|-------------|--------|
| Cu(2+)  | 6.23E-10    | 0      |
| Cu <sub>2</sub> (OH) <sub>2</sub> +2 (+2)           | 1.57E-13    | 0      |
| Cu(OH) <sub>3</sub> - (-1)                          | 3.94E-13    | 0      |
| Cu(OH) <sub>4</sub> -2 (-2)                         | 8.47E-18    | 0      |
| CuOH + (+1)   | 4.24E-10    | 0      |
| Cu(OH) <sub>2</sub> AQ                              | 7.04E-08    | 2.1    |
| CuHCO <sub>3</sub> + (+1)                           | 9.44E-11    | 0      |
| CuHPO <sub>4</sub>                                  | 2.28E-13    | 0      |
| Fe(st)OCu (+1)                                      | 0.000000668 | 19.6   |
| *Fe(wk)OCu (+1)                                     | 0.00000266  | 78.2   |
| CuCl <sub>3</sub> - (-1)                            | 9.3E-20     | 0      |
| CuCl <sub>2</sub> AQ                                | 7.63E-15    | 0      |
| CuCl <sub>4</sub> -2 1 (-2)                         | 1.42E-24    | 0      |
| CuCl + (+1)   | 5.01E-12    | 0      |
| CuCO <sub>3</sub> AQ                                | 4.03E-09    | 0      |
| Cu(CO <sub>3</sub> ) <sub>2</sub> -2 (-2)           | 1.13E-11    | 0      |
| CuSO <sub>4</sub> AQ                                | 7.53E-12    | 0      |
| ATACAMITE   | 0.000031    | *****  |
| AZURITE   | 0.000000326 | *****  |
| MALACHITE   | 0.000616    | *****  |
| TENORITE  | 0.129       | *****  |
| CU(OH) <sub>2</sub>                                 | 0.0123      | *****  |
| CUPRICFERIT   | 0.000555    | *****  |
| CU <sub>2</sub> (OH) <sub>3</sub> NO <sub>3</sub>   | 3.92E-09    | *****  |
| ANTLERITE   | 2.07E-09    | *****  |
| CUOCUSO <sub>4</sub>                                | 1.05E-18    | *****  |
| BROCHANTITE   | 6.22E-10    | *****  |
| LANGITE   | 7.41E-11    | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ,3W | 1.46E-17    | *****  |
| CHALCANTHITE  | 1.48E-11    | *****  |
| MELANOTHALLI  | 1.04E-18    | *****  |
| CUCO <sub>3</sub>                                   | 0.0000032   | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>     | 7.83E-16    | *****  |
| CUSO <sub>4</sub>                                   | 6.05E-17    | *****  |

MINEQL output for speciation of copper with considering cotribution from sediment

Location 7(Intermediate Period), Dhanmondi Lake

| Name            | Conc.       | %Total |
|-----------------|-------------|--------|
| Cu(2+)          | 2.78E-10    | 0      |
| Cu2(OH)2+2 (+2) | 7.12E-14    | 0      |
| Cu(OH)3 - (-1)  | 2.79E-12    | 0      |
| Cu(OH)4 -2 (-2) | 1.44E-16    | 0      |
| CuOH + (+1)     | 4.88E-10    | 0      |
| Cu(OH)2 AQ      | 0.000000203 | 5.8    |
| CuHCO3 + (+1)   | 1.05E-10    | 0      |
| CuHPO4          | 8.32E-14    | 0      |
| Fe(st)OCu (+1)  | 0.000000457 | 13.1   |
| *Fe(wk)OCu (+1) | 0.00000283  | 80.8   |
| CuCl3 - (-1)    | 4.33E-29    | 0      |
| CuCl2 AQ        | 3.29E-21    | 0      |
| CuCl -2 1 (-2)  | 1.19E-36    | 0      |
| CuCl + (+1)     | 1.82E-15    | 0      |
| CuCO3 AQ        | 1.12E-08    | 0      |
| Cu(CO3)2-2 (-2) | 1.8E-10     | 0      |
| CuSO4 AQ        | 1.17E-11    | 0      |
| ATACAMITE       | 4.48E-08    | *****  |
| AZURITE         | 0.00000178  | *****  |
| MALACHITE       | 0.00196     | *****  |
| TENORITE        | 0.15        | *****  |
| CU(OH)2         | 0.0143      | *****  |
| CUPRICFERIT     | 0.001       | *****  |
| CU2(OH)3NO3     | 4.72E-09    | *****  |
| ANTLERITE       | 2.86E-08    | *****  |
| CUOCUSO4        | 6.09E-19    | *****  |
| BROCHANTITE     | 2.47E-08    | *****  |
| LANGITE         | 2.8E-10     | *****  |
| CU3(PO4)2,3W    | 5.58E-18    | *****  |
| CHALCANTHITE    | 2.7E-11     | *****  |
| MELANOTHALLI    | 4.03E-25    | *****  |
| CUCO3           | 0.00000892  | *****  |
| CU3(PO4)2       | 3E-16       | *****  |
| CUSO4           | 3.44E-17    | *****  |

MINEQL output for speciation of copper with considering contribution from sediment

Location 1(Dry Period), Ramna Lake

| Name  | Conc.       | %Total |
|---|-------------|--------|
| Cu(2+)  | 3.26E-11    | 0      |
| Cu <sub>2</sub> (OH) <sub>2</sub> +2 (+2)           | 2.69E-14    | 0      |
| Cu(OH) <sub>3</sub> - (-1)                          | 5.18E-12    | 0      |
| Cu(OH) <sub>4</sub> -2 (-2)                         | 6.64E-16    | 0      |
| CuOH + (+1)   | 1.44E-10    | 0      |
| Cu(OH) <sub>2</sub> AQ                              | 0.000000151 | 4.3    |
| CuHCO <sub>3</sub> + (+1)                           | 3.25E-11    | 0      |
| CuHPO <sub>4</sub>                                  | 4.69E-14    | 0      |
| Fe(st)OCu (+1)                                      | 0.00000053  | 15.1   |
| *Fe(wk)OCu (+1)                                     | 0.00000281  | 80.3   |
| CuCl <sub>3</sub> - (-1)                            | 6.67E-22    | 0      |
| CuCl <sub>2</sub> AQ                                | 1.13E-16    | 0      |
| CuCl <sub>4</sub> -2 1 (-2)                         | 3.84E-27    | 0      |
| CuCl + (+1)   | 1.54E-13    | 0      |
| CuCO <sub>3</sub> AQ                                | 8.74E-09    | 0      |
| Cu(CO <sub>3</sub> ) <sub>2</sub> -2 (-2)           | 9.06E-10    | 0      |
| CuSO <sub>4</sub> AQ                                | 1.02E-12    | 0      |
| ATACAMITE   | 0.0000164   | *****  |
| AZURITE   | 0.00000585  | *****  |
| MALACHITE   | 0.00418     | *****  |
| TENORITE  | 0.399       | *****  |
| CU(OH) <sub>2</sub>                                 | 0.0382      | *****  |
| CUPRICFERIT   | 0.00144     | *****  |
| CU <sub>2</sub> (OH) <sub>3</sub> NO <sub>3</sub>   | 1.09E-09    | *****  |
| ANTLERITE   | 1.25E-09    | *****  |
| CUOCUSO <sub>4</sub>                                | 6.97E-19    | *****  |
| BROCHANTITE   | 8.02E-10    | *****  |
| LANGITE   | 2.49E-10    | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ,3W | 1.32E-18    | *****  |
| CHALCANTHITE  | 1.88E-12    | *****  |
| MELANOTHALLI  | 1.6E-20     | *****  |
| CUCO <sub>3</sub>                                   | 0.00000694  | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>     | 7.1E-17     | *****  |
| CUSO <sub>4</sub>                                   | 1.23E-17    | *****  |



MINEQL output for speciation of copper with considering contribution from sediment

Location 1(Wet Period), Ramna Lake

| Name            | Conc.       | %Total |
|-----------------|-------------|--------|
| Cu(2+)          | 1.75E-09    | 0      |
| Cu2(OH)2+2 (+2) | 9.85E-14    | 0      |
| Cu(OH)3 - (-1)  | 1.75E-14    | 0      |
| Cu(OH)4 -2 (-2) | 9.48E-20    | 0      |
| CuOH + (+1)     | 2.98E-10    | 0      |
| Cu(OH)2 AQ      | 1.24E-08    | 1      |
| CuHCO3 + (+1)   | 6.68E-11    | 0      |
| CuHPO4          | 2.16E-12    | 0      |
| Fe(st)OCu (+1)  | 0.000000344 | 28.6   |
| *Fe(wk)OCu (+1) | 0.000000341 | 70.1   |
| CuCl3 - (-1)    | 2.82E-21    | 0      |
| CuCl2 AQ        | 1.07E-15    | 0      |
| CuCl -2 1 (-2)  | 8.28E-27    | 0      |
| CuCl + (+1)     | 3.28E-12    | 0      |
| CuCO3 AQ        | 7.16E-10    | 0      |
| Cu(CO3)2-2 (-2) | 1.28E-13    | 0      |
| CuSO4 AQ        | 8.86E-11    | 0      |
| ATACAMITE       | 0.00000103  | *****  |
| AZURITE         | 2.51E-09    | *****  |
| MALACHITE       | 0.0000239   | *****  |
| TENORITE        | 0.028       | *****  |
| CU(OH)2         | 0.00267     | *****  |
| CUPRICFERIT     | 0.000109    | *****  |
| CU2(OH)3NO3     | 1.5E-10     | *****  |
| ANTLERITE       | 7.47E-10    | *****  |
| CUOCUSO4        | 3.47E-18    | *****  |
| BROCHANTITE     | 3.96E-11    | *****  |
| LANGITE         | 8.06E-12    | *****  |
| CU3(PO4)2,3W    | 2.32E-16    | *****  |
| CHALCANTHITE    | 1.68E-10    | *****  |
| MELANOTHALLI    | 1.48E-19    | *****  |
| CUCO3           | 0.000000568 | *****  |
| CU3(PO4)2       | 1.25E-14    | *****  |
| CUSO4           | 8.94E-16    | *****  |



MINEQL output for speciation of copper with considering contribution from sediment

Location 1(Intermediate Period), Ramna Lake

| Name  | Conc.       | %Total |
|---|-------------|--------|
| Cu(2+)  | 1.07E-08    | 0      |
| Cu <sub>2</sub> (OH) <sub>2</sub> +2 (+2)           | 4.52E-13    | 0      |
| Cu(OH) <sub>3</sub> - (-1)                          | 2.68E-14    | 0      |
| Cu(OH) <sub>4</sub> -2 (-2)                         | 9.14E-20    | 0      |
| CuOH + (+1)   | 1.15E-09    | 0      |
| Cu(OH) <sub>2</sub> AQ                              | 3.03E-08    | 0      |
| CuHCO <sub>3</sub> + (+1)                           | 2.49E-10    | 0      |
| CuHPO <sub>4</sub>                                  | 1.78E-11    | 0      |
| Fe(st)OCu (+1)                                      | 0.000000645 | 20.2   |
| *Fe(wk)OCu (+1)                                     | 0.00000251  | 78.5   |
| CuCl <sub>3</sub> - (-1)                            | 4.36E-20    | 0      |
| CuCl <sub>2</sub> AQ                                | 1.1E-14     | 0      |
| CuCl <sub>4</sub> -2 1 (-2)                         | 3.5E-25     | 0      |
| CuCl + (+1)   | 2.08E-11    | 0      |
| CuCO <sub>3</sub> AQ                                | 1.68E-09    | 0      |
| Cu(CO <sub>3</sub> ) <sub>2</sub> -2 (-2)           | 1.15E-13    | 0      |
| CuSO <sub>4</sub> AQ                                | 3.71E-10    | 0      |
| ATACAMITE   | 0.00000512  | *****  |
| AZURITE   | 6.87E-09    | *****  |
| MALACHITE   | 0.0000481   | *****  |
| TENORITE  | 0.0245      | *****  |
| CU(OH) <sub>2</sub>                                 | 0.00234     | *****  |
| CUPRICFERIT   | 0.000157    | *****  |
| CU <sub>2</sub> (OH) <sub>3</sub> NO <sub>3</sub>   | 4.43E-10    | *****  |
| ANTLERITE   | 2.02E-08    | *****  |
| CUOCUSO <sub>4</sub>                                | 3.54E-18    | *****  |
| BROCHANTITE   | 2.61E-09    | *****  |
| LANGITE   | 3.73E-11    | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ,3W | 3.82E-14    | *****  |
| CHALCANTHITE  | 8.44E-10    | *****  |
| MELANOTHALLI  | 1.36E-18    | *****  |
| CUCO <sub>3</sub>                                   | 0.00000134  | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>     | 2.05E-12    | *****  |
| CUSO <sub>4</sub>                                   | 1.21E-15    | *****  |

MINEQL output for speciation of copper with considering contribution from sediment

Location 2(Dry Period), Ramna Lake

| Name            | Conc.       | %Total |
|-----------------|-------------|--------|
| Cu(2+)          | 1.44E-11    | 0      |
| Cu2(OH)2+2 (+2) | 1.23E-14    | 0      |
| Cu(OH)3 - (-1)  | 9.09E-12    | 0      |
| Cu(OH)4 -2 (-2) | 1.92E-15    | 0      |
| CuOH + (+1)     | 9.89E-11    | 0      |
| Cu(OH)2 AQ      | 0.000000164 | 5      |
| CuHCO3 + (+1)   | 2.22E-11    | 0      |
| CuHPO4          | 5.15E-14    | 0      |
| Fe(st)OCu (+1)  | 0.000000497 | 15.1   |
| *Fe(wk)OCu (+1) | 0.00000263  | 79.6   |
| CuCl3 - (-1)    | 9.78E-23    | 0      |
| CuCl2 AQ        | 2.34E-17    | 0      |
| CuCl -2 1 (-2)  | 4.16E-28    | 0      |
| CuCl + (+1)     | 4.56E-14    | 0      |
| CuCO3 AQ        | 9.49E-09    | 0      |
| Cu(CO3)2-2 (-2) | 2.61E-09    | 0      |
| CuSO4 AQ        | 8.01E-13    | 0      |
| ATACAMITE       | 0.00000815  | *****  |
| AZURITE         | 0.00000704  | *****  |
| MALACHITE       | 0.00474     | *****  |
| TENORITE        | 0.417       | *****  |
| CU(OH)2         | 0.0399      | *****  |
| CUPRICFERIT     | 0.00153     | *****  |
| CU2(OH)3NO3     | 7.65E-10    | *****  |
| ANTLERITE       | 1.17E-09    | *****  |
| CUOCUSO4        | 5.45E-19    | *****  |
| BROCHANTITE     | 8.17E-10    | *****  |
| LANGITE         | 2.28E-10    | *****  |
| CU3(PO4)2,3W    | 1.73E-18    | *****  |
| CHALCANTHITE    | 1.49E-12    | *****  |
| MELANOTHALLI    | 3.3E-21     | *****  |
| CUCO3           | 0.00000754  | *****  |
| CU3(PO4)2       | 9.3E-17     | *****  |
| CUSO4           | 9.27E-18    | *****  |

MINEQL output for speciation of copper with considering contribution from sediment

Location 2(Wet Period), Ramna Lake

| Name            | Conc.       | %Total |
|-----------------|-------------|--------|
| Cu(2+)          | 8.23E-09    | 0      |
| Cu2(OH)2+2 (+2) | 3.64E-12    | 0      |
| Cu(OH)3 - (-1)  | 1.65E-13    | 0      |
| Cu(OH)4 -2 (-2) | 1.12E-18    | 0      |
| CuOH + (+1)     | 1.77E-09    | 0      |
| Cu(OH)2 AQ      | 0.000000093 | 3.3    |
| CuHCO3 + (+1)   | 3.97E-10    | 0      |
| CuHPO4          | 7.24E-12    | 0      |
| Fe(st)OCu (+1)  | 0.000000396 | 14.1   |
| *Fe(wk)OCu (+1) | 0.00000229  | 82     |
| CuCl3 - (-1)    | 1.8E-20     | 0      |
| CuCl2 AQ        | 6.19E-15    | 0      |
| CuCl4 -2 1 (-2) | 5.68E-26    | 0      |
| CuCl + (+1)     | 1.73E-11    | 0      |
| CuCO3 AQ        | 5.36E-09    | 0      |
| Cu(CO3)2-2 (-2) | 1.52E-12    | 0      |
| CuSO4 AQ        | 3.55E-10    | 0      |
| ATACAMITE       | 0.0000525   | *****  |
| AZURITE         | 0.00000112  | *****  |
| MALACHITE       | 0.00139     | *****  |
| TENORITE        | 0.218       | *****  |
| CU(OH)2         | 0.0208      | *****  |
| CUPRICFERIT     | 0.000831    | *****  |
| CU2(OH)3NO3     | 0.000000007 | *****  |
| ANTLERITE       | 0.000000167 | *****  |
| CUOCUSO4        | 1.14E-16    | *****  |
| BROCHANTITE     | 6.61E-08    | *****  |
| LANGITE         | 0.000000015 | *****  |
| CU3(PO4)2,3W    | 1.94E-14    | *****  |
| CHALCANTHITE    | 6.7E-10     | *****  |
| MELANOTHALLI    | 8.65E-19    | *****  |
| CUCO3           | 0.00000426  | *****  |
| CU3(PO4)2       | 1.04E-12    | *****  |
| CUSO4           | 3.75E-15    | *****  |

MINQL output for speciation of copper with considering contribution from sediment

Location 2(Intermediate Period), Ramna Laka

| Name  | Conc.       | %Total |
|---|-------------|--------|
| Cu(2+)  | 5.79E-09    | 0      |
| Cu <sub>2</sub> (OH) <sub>2</sub> +2 (+2)           | 7.58E-13    | 0      |
| Cu(OH) <sub>3</sub> - (-1)                          | 2.31E-13    | 0      |
| Cu(OH) <sub>4</sub> -2 (-2)                         | 1.98E-18    | 0      |
| CuOH + (+1)   | 1.57E-09    | 0      |
| Cu(OH) <sub>2</sub> AQ                              | 0.000000104 | 0      |
| CuHCO <sub>3</sub> + (+1)                           | 3.38E-10    | 3.8    |
| CuHPO <sub>4</sub>                                  | 7.12E-12    | 0      |
| Fe(st)OCu (+1)                                      | 0.00000036  | 0      |
| *Fe(wk)OCu (+1)                                     | 0.00000226  | 13.1   |
| CuCl <sub>3</sub> - (-1)                            | 1.12E-20    | 82.6   |
| CuCl <sub>2</sub> AQ                                | 3.59E-15    | 0      |
| CuCl <sub>4</sub> -2 1 (-2)                         | 7.43E-26    | 0      |
| CuCl + (+1)   | 8.57E-12    | 0      |
| CuCO <sub>3</sub> AQ                                | 5.74E-09    | 0      |
| Cu(CO <sub>3</sub> ) <sub>2</sub> -2 (-2)           | 2.47E-12    | 0      |
| CuSO <sub>4</sub> AQ                                | 2.48E-10    | 0      |
| ATACAMITE   | 0.0000171   | 0      |
| AZURITE   | 0.000000238 | 0      |
| MALACHITE   | 0.000512    | 0      |
| TENORITE  | 0.0768      | 0      |
| CU(OH) <sub>2</sub>                                 | 0.00733     | 0      |
| CUPRICFERIT   | 0.000512    | 0      |
| CU <sub>2</sub> (OH) <sub>3</sub> NO <sub>3</sub>   | 1.87E-09    | 0      |
| ANTLERITE   | 0.000000159 | 0      |
| CUOCUSO <sub>4</sub>                                | 6.61E-18    | 0      |
| BROCHANTITE   | 7.02E-08    | 0      |
| LANGITE   | 7.96E-10    | 0      |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ,3W | 2.09E-14    | 0      |
| CHALCANTHITE  | 5.72E-10    | 0      |
| MELANOTHALLI  | 4.39E-19    | 0      |
| CUCO <sub>3</sub>                                   | 0.00000456  | 0      |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>     | 1.12E-12    | 0      |
| CUSO <sub>4</sub>                                   | 7.29E-16    | 0      |

MINEQL output for speciation of copper with considering contribution from sediment

Location 3(Dry Period), Ramna Lake

| Name  | Conc.       | %Total |
|---|-------------|--------|
| Cu(2+)  | 0.000000013 | 0      |
| Cu <sub>2</sub> (OH) <sub>2</sub> +2 (+2)           | 1.65E-12    | 0      |
| Cu(OH) <sub>3</sub> - (-1)                          | 1.64E-14    | 0      |
| Cu(OH) <sub>4</sub> -2 (-2)                         | 4.52E-20    | 0      |
| CuOH + (+1)   | 1.11E-09    | 0      |
| Cu(OH) <sub>2</sub> AQ                              | 2.32E-08    | 0      |
| CuHCO <sub>3</sub> + (+1)                           | 2.5E-10     | 0      |
| CuHPO <sub>4</sub>                                  | 2.2E-11     | 0      |
| Fe(st)OCu (+1)                                      | 0.000000587 | 22.6   |
| *Fe(wk)OCu (+1)                                     | 0.00000197  | 75.9   |
| CuCl <sub>3</sub> - (-1)                            | 1.07E-19    | 0      |
| CuCl <sub>2</sub> AQ                                | 2.37E-14    | 0      |
| CuCl <sub>4</sub> -2 1 (-2)                         | 4.88E-25    | 0      |
| CuCl + (+1)   | 4.37E-11    | 0      |
| CuCO <sub>3</sub> AQ                                | 1.34E-09    | 0      |
| Cu(CO <sub>3</sub> ) <sub>2</sub> -2 (-2)           | 6.17E-14    | 0      |
| CuSO <sub>4</sub> AQ                                | 7.95E-10    | 0      |
| ATACAMITE   | 0.0000143   | *****  |
| AZURITE   | 2.12E-08    | *****  |
| MALACHITE   | 0.0000987   | *****  |
| TENORITE  | 0.0613      | *****  |
| CU(OH) <sub>2</sub>                                 | 0.00586     | *****  |
| CUPRICFERIT   | 0.000221    | *****  |
| CU <sub>2</sub> (OH) <sub>3</sub> NO <sub>3</sub>   | 1.25E-09    | *****  |
| ANTLERITE   | 0.000000023 | *****  |
| CUOCUSO <sub>4</sub>                                | 8.38E-17    | *****  |
| BROCHANTITE   | 2.28E-09    | *****  |
| LANGITE   | 7.07E-10    | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ,3W | 4.48E-14    | *****  |
| CHALCANTHITE  | 1.47E-09    | *****  |
| MELANOTHALLI  | 3.37E-18    | *****  |
| CUCO <sub>3</sub>                                   | 0.00000107  | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>     | 2.41E-12    | *****  |
| CUSO <sub>4</sub>                                   | 9.62E-15    | *****  |



MINEQL output for speciation of copper with considering contribution from sediment

Location 3(Wet Period), Ramna Lake

| Name   | Conc.       | %Total |
|--|-------------|--------|
| Cu(2+)   | 4.42E-10    | 0      |
| Cu <sub>2</sub> (OH) <sub>2</sub> <sup>2+</sup> (+2) | 1.65E-13    | 0      |
| Cu(OH) <sub>3</sub> <sup>-</sup> (-1)                | 5.57E-13    | 0      |
| Cu(OH) <sub>4</sub> <sup>-2</sup> (-2)               | 1.54E-17    | 0      |
| CuOH <sup>+</sup> (+1)                               | 3.75E-10    | 0      |
| Cu(OH) <sub>2</sub> AQ                               | 7.83E-08    | 3.3    |
| CuHCO <sub>3</sub> <sup>+</sup> (+1)                 | 8.41E-11    | 0      |
| CuHPO <sub>4</sub>                                   | 6.68E-14    | 0      |
| Fe(st)OCu (+1)                                       | 0.000000406 | 16.9   |
| *Fe(wk)OCu (+1)                                      | 0.00000191  | 79.6   |
| CuCl <sub>3</sub> <sup>-</sup> (-1)                  | 7.91E-22    | 0      |
| CuCl <sub>2</sub> AQ                                 | 2.87E-16    | 0      |
| CuCl <sub>4</sub> <sup>-2</sup> 1 (-2)               | 2.37E-27    | 0      |
| CuCl <sup>+</sup> (+1)                               | 8.6E-13     | 0      |
| CuCO <sub>3</sub> AQ                                 | 4.52E-09    | 0      |
| Cu(CO <sub>3</sub> ) <sub>2</sub> <sup>-2</sup> (-2) | 2.08E-11    | 0      |
| CuSO <sub>4</sub> AQ                                 | 3.46E-11    | 0      |
| ATACAMITE  | 0.00000876  | *****  |
| AZURITE  | 0.00000067  | *****  |
| MALACHITE  | 0.00099     | *****  |
| TENORITE   | 0.183       | *****  |
| CU(OH) <sub>2</sub>                                  | 0.0175      | *****  |
| CUPRICFERIT  | 0.0007      | *****  |
| CU <sub>2</sub> (OH) <sub>3</sub> NO <sub>3</sub>    | 1.24E-09    | *****  |
| ANTLERITE  | 1.15E-08    | *****  |
| CUOCUSO <sub>4</sub>                                 | 9.35E-18    | *****  |
| BROCHANTITE  | 3.85E-09    | *****  |
| LANGITE  | 8.72E-10    | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ·3W  | 1.39E-18    | *****  |
| CHALCANTHITE   | 6.53E-11    | *****  |
| MELANOTHALLI   | 4.02E-20    | *****  |
| CUCO <sub>3</sub>                                    | 0.00000359  | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>      | 7.48E-17    | *****  |
| CUSO <sub>4</sub>                                    | 3.65E-16    | *****  |

MINEQL output for speciation of copper with considering contribution from sediment

Location 3(Intermediate Period), Ramna Lake

| Name  | Conc.       | %Total |
|---|-------------|--------|
| Cu(2+)  | 8.35E-09    | 0      |
| Cu <sub>2</sub> (OH) <sub>2</sub> +2 (+2)           | 1.38E-12    | 0      |
| Cu(OH) <sub>3</sub> - (-1)                          | 3.33E-13    | 0      |
| Cu(OH) <sub>4</sub> -2 (-2)                         | 3.72E-18    | 0      |
| CuOH + (+1)   | 1.98E-09    | 0      |
| Cu(OH) <sub>2</sub> AQ                              | 0.000000131 | 0      |
| CuHCO <sub>3</sub> + (+1)                           | 4.27E-10    | 2.9    |
| CuHPO <sub>4</sub>                                  | 2.32E-13    | 0      |
| Fe(st)OCu (+1)                                      | 0.000000584 | 0      |
| *Fe(wk)OCu (+1)                                     | 0.00000377  | 13     |
| CuCl <sub>3</sub> - (-1)                            | 7.49E-21    | 83.7   |
| CuCl <sub>2</sub> AQ                                | 2.72E-15    | 0      |
| CuCl <sub>4</sub> -2 1 (-2)                         | 5.04E-26    | 0      |
| CuCl + (+1)   | 8.38E-12    | 0      |
| CuCO <sub>3</sub> AQ                                | 7.25E-09    | 0      |
| Cu(CO <sub>3</sub> ) <sub>2</sub> -2 (-2)           | 4.65E-12    | 0      |
| CuSO <sub>4</sub> AQ                                | 1.42E-10    | 0      |
| ATACAMITE   | 0.0000211   | *****  |
| AZURITE   | 0.000000478 | *****  |
| MALACHITE   | 0.000816    | *****  |
| TENORITE  | 0.0969      | *****  |
| CU(OH) <sub>2</sub>                                 | 0.00925     | *****  |
| CUPRICFERIT   | 0.000647    | *****  |
| CU <sub>2</sub> (OH) <sub>3</sub> NO <sub>3</sub>   | 2.6E-09     | *****  |
| ANTLERITE   | 0.000000144 | *****  |
| CUOCUSO <sub>4</sub>                                | 4.77E-18    | *****  |
| BROCHANTITE   | 8.06E-08    | *****  |
| LANGITE   | 9.14E-10    | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ,3W | 2.81E-17    | *****  |
| CHALCANTHITE  | 3.27E-10    | *****  |
| MELANOTHALLI  | 3.33E-19    | *****  |
| CUCO <sub>3</sub>                                   | 0.00000576  | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>     | 1.51E-15    | *****  |
| CUSO <sub>4</sub>                                   | 4.16E-16    | *****  |

MINEQL output for speciation of copper with considering contribution from sediment

Location 4(Dry Period), Ramna Lake

| Name  | Conc.       | %Total |
|---|-------------|--------|
| Cu(2+)  | 1.22E-11    | 0      |
| Cu <sub>2</sub> (OH) <sub>2</sub> +2 (+2)           | 8.88E-15    | 0      |
| Cu(OH) <sub>3</sub> - (-1)                          | 7.73E-12    | 0      |
| Cu(OH) <sub>4</sub> -2 (-2)                         | 1.64E-15    | 0      |
| CuOH + (+1)   | 8.38E-11    | 0      |
| Cu(OH) <sub>2</sub> AQ                              | 0.000000139 | 4.1    |
| CuHCO <sub>3</sub> + (+1)                           | 1.88E-11    | 0      |
| CuHPO <sub>4</sub>                                  | 4.36E-14    | 0      |
| Fe(st)OCu (+1)                                      | 0.000000534 | 15.7   |
| *Fe(wk)OCu (+1)                                     | 0.00000272  | 79.9   |
| CuCl <sub>3</sub> - (-1)                            | 9.26E-23    | 0      |
| CuCl <sub>2</sub> AQ                                | 2.13E-17    | 0      |
| CuCl <sub>2</sub> -2 1 (-2)                         | 4.11E-28    | 0      |
| CuCl + (+1)   | 4E-14       | 0      |
| CuCO <sub>3</sub> AQ                                | 8.04E-09    | 0      |
| Cu(CO <sub>3</sub> ) <sub>2</sub> -2 (-2)           | 2.23E-09    | 0      |
| CuSO <sub>4</sub> AQ                                | 8.04E-13    | 0      |
| ATACAMITE   | 0.00000606  | *****  |
| AZURITE   | 0.00000428  | *****  |
| MALACHITE   | 0.0034      | *****  |
| TENORITE  | 0.353       | *****  |
| CU(OH) <sub>2</sub>                                 | 0.0338      | *****  |
| CUPRICFERIT   | 0.0013      | *****  |
| CU <sub>2</sub> (OH) <sub>3</sub> NO <sub>3</sub>   | 5.48E-10    | *****  |
| ANTLERITE   | 8.4E-10     | *****  |
| CUOCUSO <sub>4</sub>                                | 4.64E-19    | *****  |
| BROCHANTITE   | 4.98E-10    | *****  |
| LANGITE   | 1.39E-10    | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ,3W | 1.05E-18    | *****  |
| CHALCANTHITE  | 1.5E-12     | *****  |
| MELANOTHALLI  | 3.01E-21    | *****  |
| CUCO <sub>3</sub>                                   | 0.00000639  | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>     | 5.65E-17    | *****  |
| CUSO <sub>4</sub>                                   | 9.3E-18     | *****  |

MINEQL output for speciation of copper with considering contribution from sediment

Location 4(Wet Period), Ramna Lake

| Name            | Conc.       | %Total |
|-----------------|-------------|--------|
| Cu(2+)          | 1.59E-09    | 0      |
| Cu2(OH)2+2 (+2) | 2.06E-13    | 0      |
| Cu(OH)3 - (-1)  | 6.33E-14    | 0      |
| Cu(OH)4 -2 (-2) | 5.34E-19    | 0      |
| CuOH + (+1)     | 4.33E-10    | 0      |
| Cu(OH)2 AQ      | 2.86E-08    | 0      |
| CuHCO3 + (+1)   | 9.7E-11     | 1.5    |
| CuHPO4          | 9.74E-13    | 0      |
| Fe(st)OCu (+1)  | 0.000000475 | 0      |
| *Fe(wk)OCu (+1) | 0.00000139  | 25     |
| CuCl3 - (-1)    | 6.98E-21    | 73.3   |
| CuCl2 AQ        | 1.9E-15     | 0      |
| CuCl4 -2 1 (-2) | 2.81E-26    | 0      |
| CuCl + (+1)     | 4.19E-12    | 0      |
| CuCO3 AQ        | 1.65E-09    | 0      |
| Cu(CO3)2-2 (-2) | 7.21E-13    | 0      |
| CuSO4 AQ        | 8.69E-14    | 0      |
| ATACAMITE       | 0.0000048   | *****  |
| AZURITE         | 3.06E-08    | *****  |
| MALACHITE       | 0.000127    | *****  |
| TENORITE        | 0.0643      | *****  |
| CU(OH)2         | 0.00615     | *****  |
| CUPRICFERIT     | 0.00025     | *****  |
| CU2(OH)3NO3     | 5.07E-10    | *****  |
| ANTLERITE       | 3.88E-12    | *****  |
| CUOCUSO4        | 7.82E-21    | *****  |
| BROCHANTITE     | 4.73E-13    | *****  |
| LANGITE         | 9.63E-14    | *****  |
| CU3(PO4)2,3W    | 1.08E-16    | *****  |
| CHALCANTHITE    | 1.65E-13    | *****  |
| MELANOTHALLI    | 2.65E-19    | *****  |
| CUCO3           | 0.00000131  | *****  |
| CU3(PO4)2       | 5.8E-15     | *****  |
| CUSO4           | 8.77E-19    | *****  |

MINEQL output for speciation of copper with considering contribution from sediment

Location 4(Intermediate Period), Ramna Lake

| Name  | Conc.       | %Total |
|---|-------------|--------|
| Cu(2+)  | 3.63E-08    | 0      |
| Cu <sub>2</sub> (OH) <sub>2</sub> +2 (+2)           | 1.88E-11    | 0      |
| Cu(OH) <sub>3</sub> - (-1)                          | 7.25E-13    | 0      |
| Cu(OH) <sub>4</sub> -2 (-2)                         | 4.94E-18    | 0      |
| CuOH + (+1)   | 7.81E-09    | 0      |
| Cu(OH) <sub>2</sub> AQ                              | 0.00000041  | 0      |
| CuHCO <sub>3</sub> + (+1)                           | 1.68E-09    | 7.3    |
| CuHPO <sub>4</sub>                                  | 6.11E-11    | 0      |
| Fe(st)OCu (+1)                                      | 0.000000374 | 0      |
| *Fe(wk)OCu (+1)                                     | 0.00000475  | 6.7    |
| CuCl <sub>3</sub> - (-1)                            | 4.85E-20    | 84.8   |
| CuCl <sub>2</sub> AQ                                | 1.76E-14    | 0      |
| CuCl <sub>4</sub> -2 1 (-2)                         | 2.86E-25    | 0      |
| CuCl + (+1)   | 4.75E-11    | 0      |
| CuCO <sub>3</sub> AQ                                | 2.27E-08    | 0      |
| Cu(CO <sub>3</sub> ) <sub>2</sub> -2 (-2)           | 6.17E-12    | 0      |
| CuSO <sub>4</sub> AQ                                | 1.82E-09    | 0      |
| ATACAMITE   | 0.000298    | 0      |
| AZURITE   | 0.0000147   | *****  |
| MALACHITE   | 0.008       | *****  |
| TENORITE  | 0.303       | *****  |
| CU(OH) <sub>2</sub>                                 | 0.029       | *****  |
| CUPRICFERIT   | 0.00202     | *****  |
| CU <sub>2</sub> (OH) <sub>3</sub> NO <sub>3</sub>   | 3.67E-08    | *****  |
| ANTLERITE   | 0.0000182   | *****  |
| CU <sub>2</sub> (OH) <sub>3</sub> NO <sub>3</sub>   | 1.91E-16    | *****  |
| BROCHANTITE   | 0.0000317   | *****  |
| LANGITE   | 0.00000036  | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> .3W | 6.1E-12     | *****  |
| CHALCANTHITE  | 4.19E-09    | *****  |
| MELANOTHALLI  | 2.15E-18    | *****  |
| CUCO <sub>3</sub>                                   | 0.000018    | *****  |
| CU <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>     | 3.27E-10    | *****  |
| CUSO <sub>4</sub>                                   | 5.34E-15    | *****  |

