

CHAPTER I



INTRODUCTION

Although heavy metals are trace elements, they do play an important role to aquatic organisms. Some metals are essential for the growth of aquatic life but some are toxic. The uptake of trace metals depends on their chemical states in the aquatic system. Among metals that could affect the aquatic environment, the present study will deal only with cadmium, lead and copper.

1.1 Sources of Heavy Metals in the Aquatic Environment

The modes of entry of cadmium, lead and copper into aquatic environment are not well understood. They are generally classified into two main categories, namely, natural sources and artificial sources. Atmospheric fallouts, upland river flows, leaching from soil and destruction of mineral ores are important natural sources, but the most important one is from artificial sources. The uses of various forms of cadmium, lead and copper in industries and in agriculture result in increasing of artificial sources, especially direct discharge of industrial and domestic waste into waterways. Kenneth and Roadney(1) reported that the lead aerosol concentration in some coastal metropolitans in California was about 100 ng.cm^{-3} and their concentrations were higher during the occurrence of smog. By using tracer technique, Chow and

co-workers(2) showed that the lead accumulation in sediment cores from Baja California province could be derived from lead additives such as those present in the type of gasoline sold in Southern California. It was claimed that on a daily basis, 0.5 ton of lead was injected into the zone of California by atmospheric fallout, 0.55 ton of lead was discharged through municipal waste outfalls and 0.24 ton from the average storm and river runoff. The work of Erlenkeuser et al.(3) in the Baltic Sea showed that a number of other metals released by the burning of fossil fuels were enriched in marine sediments via atmospheric fallouts.

Menasveta and Sawangwong(4,5) studied the distribution of heavy metals from 9 stations along the Chao Phraya River estuary. They found that dissolved copper had a maximum value of $5.50 \mu\text{g} \cdot \text{dm}^{-3}$ at station in the vicinity of the river mouth and a high total concentration of copper also found at the station which was in the Bangkok metropolitan area. From these findings it may be concluded that Bangkok city and its industrial area in the southern suburbs did contribute a significant amount of copper to the river estuary resulted in a high copper concentration. For cadmium, the maximum dissolved concentration was $0.70 \mu\text{g} \cdot \text{dm}^{-3}$ at the station in the Bangkok metropolitan area and a high total cadmium concentration was detected at almost every station. Industrial and domestic wastes were presumed to be sources that contributed cadmium to the Chao Phraya River. They also found that $5.20 \mu\text{g} \cdot \text{dm}^{-3}$ of the dissolved lead were detected at the station closed to Bangkok. The maximum total lead content was found in the Bangkok metropolitan area which also located in the area of heavy cross-river transportation

at ebb tide. The sources and pathways of lead might be lead contaminated runoff, atmospheric fallout, and direct disposal of industrial and domestic wastes. They claimed that approximately one ton of lead per day was being released to the atmosphere of Bangkok through car exhausts. A large portion of this amount of lead eventually reached the Chao Phraya River by runoff. This amount of lead coupled with the leaded gasoline exhausts from boats could contaminate certain samples as could be varified from the high values of lead found at stations located in areas of urbanization and heavy water transportation. Heavy metals in the upper part of the Gulf of Thailand were studied by Piyakarnchana and co-workers (6). They found no change in concentration of lead in sample collected in 1975 and 1976 but significant changes in concentration of cadmium and mercury were obvious. The causes of these changes were not well understood. In fact these metals entered the Gulf of Thailand from river runoff approximately $2.2 \times 10^{11} \text{ m}^3$ of water per year from which $1 \times 10^6 \text{ m}^3$ were from the Chao Phraya River. The amount of heavy metals in the upper Gulf of Thailand and the four main rivers entered it i.e. the Chao Phraya, the Bang Pakong, the Mae Khlong, the Tha Chin, had also been reported by Asian Institute of Technology (7). Different station as well as different sampling time caused great variations in concentrations of cadmium, lead and copper. In the Tha Chin River concentrations of cadmium, lead and copper were 0-50.6, 9.7-223.3 and 0.2-37.4 $\mu\text{g. dm}^{-3}$ respectively.

1.2 Toxicity of Cadmium, Lead and Copper to Aquatic Life

Cadmium, lead and copper are inorganic substances to which aquatic organisms are particularly sensitive due to the effects they have on their vital biochemical processes. Aside from the nature and concentration of metals, their toxicity to fish are affected by many factors among them are the nature and condition of fish. The species, age and general condition of fish will affect their metabolic and excretory capabilities. Fish also exhibit avoidance reaction to specific metals and their ability to detect and avoid them has been shown in Donal's(8). Trace metals from water may be absorbed across the entire body surface of fish as well as gills. Accumulation of trace metals by fish depend on size, age, species, sex and environment of fish. Hardness of water has been shown to decrease the toxicity of some metals to fish.

Eaton and co-workers(9) studied the toxicity of cadmium to embryos and larvae of seven freshwater fish species. The embryos and larvae were exposed to low concentration of cadmium in soft water. All species were killed or their growth retarded by 4 to $12 \mu\text{g Cd}\cdot\text{dm}^{-3}$. Patrick(10) studied the effect of lead and copper ions on *Brachydomio rerio* eggs and larvae and has shown that the presence of lead ions in distilled water induced epithelioma and that copper ions cause spirality of the nervous system. But lead ions suppressed abnormality and inhibitory tendency due to copper. The presence of added lead ions resulted in poor resorption of yolk in the fry, erosion of tail and fin,

spinal curvatures and out-growths from the fry which appeared to be epitheliomas. Both lead and copper ions affected successful hatching which was assessed by the ability of the prolarvae to break out the egg shells partially or fully and swim about.

The physiochemical properties of the elements and the quality of the water both play roles in governing the outcome of the ecological deterioration of water. Different forms of the same element react differently with biological and geochemical species coexisting in the water. The toxicity of heavy metals to aquatic organisms have been shown to be a function of the activity of certain chemical species rather than total metal concentration. Metal ions in particular have been shown to exert detrimental effects on a wide range of organisms. Steemann-Nielsen and Wium-Anderson(11) found that ionic copper reduced growth and photosynthesis in the green algae and diatom at concentration of total copper found in natural water and concluded that copper toxicity in aquatic system was reduced by complexation. By altering pH and chelator concentration, Sunda and Guillard(12) also linked growth inhibition and cell copper content in the marine diatom to copper(II) ion activity. Anderson and Morel(13) noted similar growth inhibition by varying the copper(II) ion activity in artificial seawater medium with the chelators tris(hydroxymethyl)aminomethane (Tris) and ethylenediaminetetraacetic acid(EDTA). Andrew et al.(14) found a direct correlation between copper(II) ion activities and mortality rates in *Daphnia magna*, as did Pagenkopf et al.(15) in the fathead minnow and rainbow trout.

Biesinger et al. (16) reported a decrease in the toxicity of copper and zinc to *Daphnia magna* when chelated by nitrilotriacetate (NTA). Branica et al. (17) found no significant uptake of iron, manganese, zinc, copper, lead or chromium by *Chironomus tentans* in the presence of NTA, EDTA and TPP (sodium tripolyphosphate). Contradicted conclusions were found in two studies on the effects of copper hydroxy complexes. Pagenkopf et al. (14) concluded that CuOH^+ and $\text{Cu}(\text{OH})_2$ probably were not toxic to fathead minnow or rainbow trout, while Andrew et al. (13) found that *Daphnia magna* mortalities increased with increasing $\text{Cu}(\text{OH})_n$ activities.

Dodge and Theis (18) further studied the uptake of different copper species e.g. copper(II) ion (Cu^{2+}), copper hydrolysis product ($\text{Cu}(\text{OH})_2$), copper glycine ($\text{Cu}(\text{Gly})_2$) and copper nitriloacetic acid (CuNTA^-) by larvae of the midge *Chironomus tentans*. The copper uptake trends indicated that chemical speciation plays an important role. The formation of very stable complexes of copper prevented uptake, while cupric ion and weakly complexed copper (with OH^-) were readily sorbed.

Sunda et al. (19) studied the effect of chemical speciation on toxicity of cadmium to grass shrimp, *Palaemonetes pugio*. They found that the survival of shrimp showed a strong correlation with the measured concentration of free cadmium ions, independent of cadmium concentration, salinity or chelator concentrations. This finding could be explained entirely in terms of the effect of salinity, chelator concentrations on the concentration of free cadmium ion. Chloride or NTA complexes of cadmium did not appear to be toxic to grass shrimp.

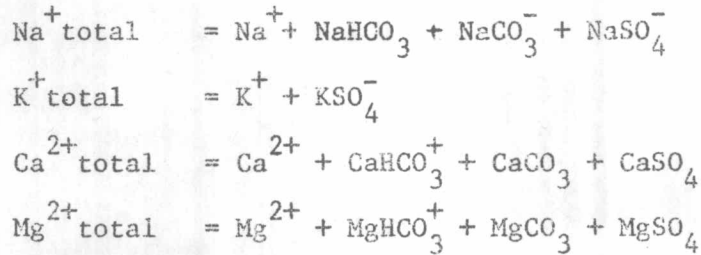
It is obvious from what have been described that the toxicity of metal to aquatic organisms relates closely to its speciation, hence several models with different proposed conditions necessary for the formation of various forms of heavy metal in sea water have been developed. Such conditions as total concentration of metal in question, pH, alkalinity, concentration of natural chelators etc. all can affect the concentration of free ions and consequently the response of organisms to that metal. The models were used with some success as can be seen from the following section.

1.3 Previous Works

Garrels and Thompson(20) had developed a chemical model for sea water of chlorinity 19‰ from available thermodynamic data. Such data were obtainable from the calculated degree of complexation between the major dissolved species present in sea water. Eight species of Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , HCO_3^- , CO_3^{2-} and SO_4^{2-} were concerned. Thermodynamic dissociation constants were used in conjunction with estimated value for individual ion activity coefficient to obtain the concentration of all species presented at the quantity exceeding a percent or two of the total. Davies(21) reported that none of the listed cations interacts strongly with chloride ion. Dissociation constants for NaOH and KOH are large; whereas those for CaOH^+ and MgOH^+ are smaller and become negligible at pH values of 8.5. In the previous work of Garrels, Thompson and Siever(22), they assumed the absence of any association between K^+ and HCO_3^- or CO_3^{2-} , and found that the assumption led to useful and

consistent results within the limit of error of ± 10 percent of the activity coefficients. They also found that interactions of those cations with HCO_3^- and CO_3^{2-} in solutions of NaCl , MgCl_2 , CaCl_2 and mixtures of them which resembling sea water did not require the assumption of complexes of a higher degree of association other than ion pairs. Values for the dissociation constants for sulphate were taken from Davies' (21). No evidence of sulphate complexes other than ion pairs has also been found.

The total concentration of each cation(20) was represented by the followings:



Because the dissociation constants of the ion pairs were given in terms of the activities of the species involved, it was therefore necessary to know the activity coefficient of the individual ion in order to convert each concentration to ion activity by the relation $a_i = m_i \gamma_i$, where a_i was the activity, γ_i the activity coefficient and m_i the molarity of ion i . Using the relationship $\gamma_{\pm}^{\nu} = \gamma_1^{\nu_1} \gamma_2^{\nu_2}$ and the assumption that $\gamma_{\text{K}^+} = \gamma_{\text{Cl}^-} = \gamma_{\pm \text{KCl}}$ they arrived at the following results :

$$\begin{aligned} \gamma_{\text{HCO}_3^-} &= \frac{\gamma_{\pm \text{KHCO}_3}^2}{\gamma_{\pm \text{KCl}}} \\ \gamma_{\text{CO}_3^{2-}} &= \frac{\gamma_{\pm \text{K}_2\text{CO}_3}^3}{\gamma_{\pm \text{KCl}}^2} \end{aligned}$$

$$\gamma_{\text{SO}_4^{2-}} = \frac{\gamma_{\pm \text{K}_2\text{SO}_4}^3}{\gamma_{\pm \text{KCl}}^2}$$

$$\gamma_{\text{Ca}^{2+}} = \frac{\gamma_{\pm \text{CaCl}_2}^3}{\gamma_{\pm \text{KCl}}^2}$$

$$\gamma_{\text{Mg}^{2+}} = \frac{\gamma_{\pm \text{MgCl}_2}^3}{\gamma_{\pm \text{KCl}}^2}$$

$$\gamma_{\text{Na}^+} = \frac{\gamma_{\pm \text{NaCl}}^2}{\gamma_{\pm \text{KCl}}}$$

The γ_{KCl} were taken from Harned and Owen(23) and those of KHCO_3 and K_2CO_3 were from Walker, Bray and Jonntson(24) whereas the values of $\gamma_{\text{Ca}^{2+}}$, $\gamma_{\text{Mg}^{2+}}$ were given by Latimer(25) at the ionic strength of sea water, approximately 0.7. From these calculations, the distribution of various forms were obtained as shown in Table 1.1.

The general picture that emerged was that the major cations in sea water exist chiefly as uncomplexed species. Magnesium ion was the major ion with regarding to its effectiveness in complexing anions. On the other hand, the anions except Cl^- , were strongly complexed, most of CO_3^{2-} , one third of HCO_3^- , and nearly half of SO_4^{2-} were paired with various cations.

Table 1.1 Distribution of major dissolved species in sea water of
chlorinity 19%

Ion	%Free Ion	%Me-SO ₄ Pair ⁴	%Me-HCO ₃ Pair ³	%Me-CO ₃ Pair ³	%Ca-anion Pair	%Mg-anion Pair	%Na-anion Pair	%K-anion Pair
Ca ²⁺	91	8	1	0.2	-	-	-	-
Mg ²⁺	87	11	1	0.3	-	-	-	-
Na ⁺	99	1.2	0.01	-	-	-	-	-
K ⁺	99	1	-	-	-	-	-	-
SO ₄ ²⁻	54	-	-	-	3	21.5	21	0.5
HCO ₃ ⁻	69	-	-	-	4	19	8	-
CO ₃ ²⁻	9	-	-	-	7	67	17	-

Goldberg(26) suggested that the model of Garrels and Thompson could be applied to trace elements in sea water and he has calculated the degree of interaction between Cd²⁺ and the anion Cl⁻ and SO₄²⁻ as examples. The total cadmium was assumed to equal the summation of Cd²⁺, CdCl⁺ and CdSO₄. From the calculation about 80 percent of cadmium ion exist as CdCl⁺. Zirino and Yamamoto(27) expanded the approach developed by Garrels and Thompson(20) to include higher order complexes and the modified model applied to the divalent metal ions of copper, cadmium, zinc and lead in sea water. The model was used to calculate the degree of interaction between each of the metal ions and the anion Cl⁻, SO₄²⁻, HCO₃⁻, CO₃²⁻, and OH⁻ as a function of pH. Interaction between a certain cation with a certain anion

was assumed to result only in the formation of complexes with coordination numbers of 1 to 4; polynuclear and mixed ligand complexes were not considered. To calculate the distribution of chemical species, a mass balance equation was written for each metal under consideration. Thus, for any given metal M:

$$[M]_{\text{total}} = [M] + \sum_{n=1}^4 \sum_{i=1}^j [ML_{(i)}_n]$$

where $[M]_{\text{total}}$ = total metal concentration
 $[M]$ = uncomplexed and/or hydrated metal ion concentration
 $[ML_{(i)}_n]$ = concentration of the n^{th} order complex between the metal M and the i^{th} ligand $L_{(i)}$
 j = total number of anions included in the model.

The concentration of the complex $ML_{(i)}_n$ can be expressed in terms of its overall formation constant, $\beta_{(i)}_n$, the uncomplexed ligand and uncomplexed metal ion concentrations and their respective activity coefficients, and activity coefficients of the complexes. Thus

$$[ML_{(i)}_n] = \beta_{(i)}_n [M] [L_{(i)}]^n \frac{\gamma_M \gamma_{L_{(i)}}^n}{\gamma_{ML_{(i)}_n}}$$

where $\beta_{(i)}_n$ = overall formation constant for the complex $ML_{(i)}_n$
 γ_M = activity coefficient of the uncomplexed metal ion M
 $\gamma_{L_{(i)}}$ = activity coefficient of the uncomplexed ligand $L_{(i)}$
 $\gamma_{ML_{(i)}_n}$ = activity coefficient of the complex $ML_{(i)}_n$

Values of the individual ionic activity coefficient of anions were taken from Garrels and Thompson(20) and individual activity coefficients for the metal

ions and their complexes were calculated from the Davies modification of Debye-Hückel expression(28)

$$\log \gamma_Z = -0.51 Z^2 \frac{\sqrt{I}}{1+\sqrt{I}} - 0.30 I$$

where Z is the ion charge and I is the ionic strength. It has to bear in mind however that this expression can only be used satisfactorily up to 0.1 ionic strength(29) with an error that seldom exceeds 2 percent and usually is smaller. Hence the modified form of Debye-Hückel was found unsuitable for the model suggested by Zirino and Yamamoto for sea water of ionic strength 0.68. It is generally known in the field of electrochemistry that for a higher concentration of electrolyte, or higher ionic strength, the complete Debye-Hückel equation is recommended(30,31). For sodium chloride solution, the suitable equation for the computation of γ_Z is

$$\log \gamma_Z = \frac{-0.5115Z^2\sqrt{I}}{1+1.316\sqrt{I}} + 0.055 I$$

In Zirino and Yamamoto's model for the chemical speciation of heavy metals in sea water, values of the formation constant of each metal-ligand were obtained from Sillen and Martell(32). The calculations showed that all four metals studied were complexed to a considerable extent in sea water ; with the exception of cadmium ion, the distribution of chemical species of the metals were found to be pH dependence, Cu^{2+} interacts primarily with OH^- and CO_3^{2-} , Zn^{2+} with OH^- , Pb^{2+} with CO_3^{2-} and Cl^- , and Cd^{2+} with Cl^- ; complexes with high coordination numbers (i.e.3 and 4) were not formed to any appreciable extent in sea water. Dyrssen and Wedborg(33)

also calculated speciation of copper, zinc, cadmium, mercury and lead ions in standard sea water using the formation constants obtained from Sillen and Martell and Supplement (32,34). The calculations included complexation of metals with -OHCl^{2-} , Br^- , F^- and glycine. Results indicated that complexations with F^- , Br^- and glycine were negligible except for mercury which forms very strong complexes with bromide ion and the interaction of metals with -OHCl^{2-} were important and should be included.

Another idea for chemical speciation of heavy metals in sea water is the existence of labile and bound metals. Technique of anodic stripping voltammetry has commonly been applied to show primary distinction between "labile" and "bound" metals in filtered water samples (35,36) at different pH. Labile metal, defined by the experimental conditions, includes ionic as well as some dissociable complexed metal, while bound metal is that fraction of the total metal content which is not labile.

In the past, only quantitative studies of heavy metals in aquatic system in Thailand received much interest. A study of their speciations, though is equally important is non-existent. In the present study, the model for chemical speciation of heavy metals in sea water is applied to the speciation of copper, lead and cadmium in the Tha Chin River estuary. Cadmium, lead and copper are chosen for this study simply because their ions are toxic. Moreover their presence and concentrations can be detected and determined simultaneously by the not so complicated technique namely the anodic stripping voltammetry. As for the choice of the sampling site, it was governed by the consideration that at the estuary, the interface between the ocean and the rivers, there usually are measurable changes

in pH, ionic strength and chemical composition of water all of which facilitate the study of chemical speciation of metals. It should be noted, however, that such properties differ greatly from one estuary to the other's. There are four main rivers enter the Gulf of Thailand and the Tha Chin River was chosen since she provides not too large the sample size for the study.