CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

1.1 Introduction

Songkhla Lake is the largest lagoon in Thailand having a surface area of 1,042 km^2. The Lake system comprises of 4 parts; Thale Noi, Inner Songkhla Lake, Middle Songkhla Lake and Outer Songkhla Lake. The Outer Songkhla Lake is situated in the lower part of Songkhla Lake covering an area of 176 km^2. It receives water from the Middle lake and surrounded watershed (Figure 1-1). It is connected to the Gulf of Thailand via a narrow channel where tidal current plays an important role in controlling water salinity.

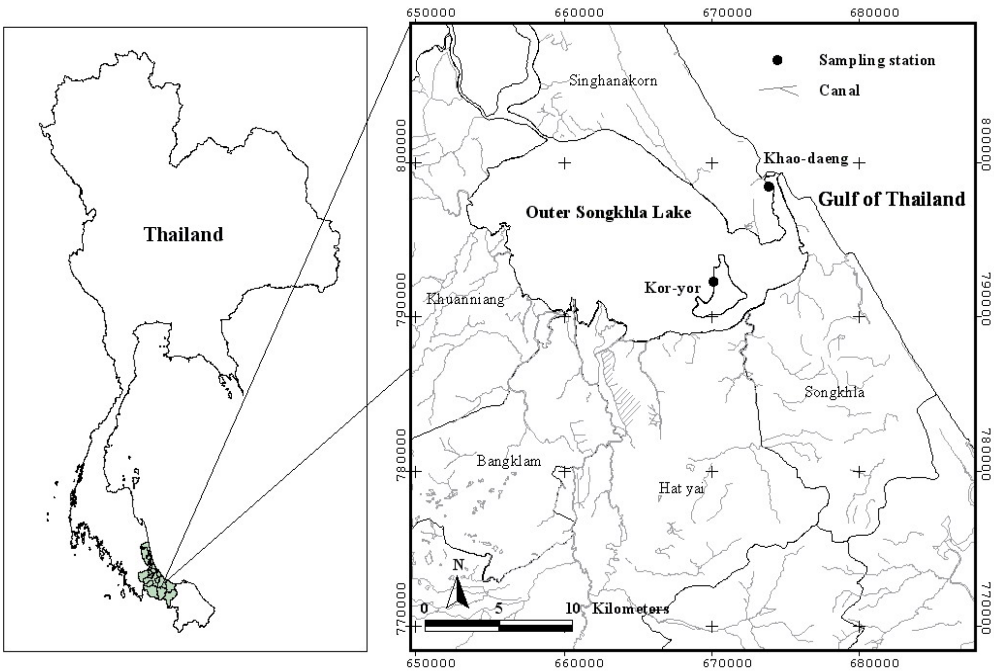

Figure 1- 1 Location of the Outer Songkhla Lake

The Outer Songkhla Lake receives pollutants from human activities via domestic sewage, agricultural drainage and industrial wastes. These pollutants are transported to the lake through rivers and atmosphere. These inputs are suspected to cause a progressively declined the quality of the lagoon ecosystem. Significant amounts of these pollutants are accumulated in sediments, which may constitute a potential source of secondary pollution. Suspended particulate matter acts as a scavenger of dissolved metals resulting in the removal of discharged contaminants from the water body to the sediment. Although sediments act as a sink for metals, it is also possible to be a source of contaminants (Sompongchaiyakul, 1989; Sirinawin *et al.,* 1998). Metals associated with sediment undergo diagenetic processes which may redissolve the metals back into pore-water, from where diffusional fluxes occur. Diffusional fluxes resulting from the concentration gradient at the sediment-water interface may transport these dissolved contaminants from the sediments to overlying water. Diffusional fluxes can be computed using Fick's First Law when the concentration gradient at the sediment-water interface is known and proper correction of the diffusion coefficients. However, this method gives an indirect estimation of the diffusional flux, and is not able to quantify the role of bioturbation or mechanical mixing of the sediments (Ciceri *et al.,* 1992).

Directed measurements of sediment–water solute exchange can be obtained by using a benthic chamber which is a device that is placed on the sediment, enclosing a known area of the sediment surface together with a known volume of ambient overlying bottom water. Fluxes of solutes at the sediment-water interface were calculated from concentration changes in the enclosed overlying water as a function of time. Fluxes of element through sediment-water interface, so-called benthic fluxes, affect elemental concentrations in both pore waters and overlying bottom waters. Thus, they are important processes of biogeochemical cycles of elements in the lake (Duarte and Flegal, 1994; Riedel *et al*., 1997). Processes responsible for these benthic fluxes are usually the upward flow of pore water caused by hydrostatic pressure, molecular diffusion due to concentration gradients e.g. concentrations in pore waters are generally higher than in overlying waters, and mixing of sediment and water at the interface due to bioturbation and water turbulence (Petersen *et al*., 1997).

The Outer Songkhla Lake is estuarine in character. As being a shallow lake, the light can penetrate the overlying water to the sediment surface; this may affect the biological processes as well as metals dynamics in the system (Woodruff *et al.,* 1999). The distribution of metals in estuary is influent by many processes such as sorption/desorption, precipitation/solubilization, coagulation, flocculation and complexation (Förstner and Wittmann, 1981).

In this study, the mobility of cadmium (Cd), copper (Cu) and lead (Pb) at sediment-water interface was investigated. These elements exhibit different geochemical properties. According to ligand-binding characteristics, copper and lead are classified as borderline A-type (tend to form stronger complexes with ligands containing F, O and N in that order) while cadmium is borderline B-type (tend to form stronger complexes with S, Cl, N, O and F in that order) (Turner *et al.,* 1981). To assess the mobility of trace metals between sediments and water, the measurements of benthic fluxes are performed by installing two types of lab-built benthic chamber; translucent (light) and dark chambers, at the lake bottom. Iron (Fe) and manganese (Mn) were also examined because their behaviors give strong indicators of changing redox conditions (Ridel *et al*., 1997).

1.2 Trace metals in estuarine lake

1.2.1 Inputs of trace metals to lakes

The major routes of heavy metals entering the lake are via riverine influx, atmospheric deposition, and anthropogenic activities. Natural occurring of metals in river water originates from the weathering rocks and leaching of soils and, hence depends in part on the occurrence of metals and ore-bearing deposits in the drainage area. Anthropogenic inputs are domestic sewage, agricultural drainage and various wastes from industrial areas. The relative importance of these different sources depends on the ration of surface area of the lake (accessible to direct atmospheric deposition) to the watershed area and river water inflow, as well as on the relative concentrations in these different inputs. Dissolved trace metals found in Songkla Lake (Thailand) are in the range of 0.009-0.34 nmol L^{-1} for Cd, 0.66-8.83

nmol L^{-1} for Cu and 0.014-1.30 nmol L^{-1} for Pb (Sirinawin *et al*., 1998). Similar trace metals concentration is found in Balaton Lake (Hungary); they are in the range of 0.009-0.044 nmol L^{-1} for Cd, 3.46-9.29 nmol $L^{-1}$for Cu and 0.193-1.59 nmol $L^{-1}$for Pb (Nguyen *et al*., 2005).

1.2.2 Regulation of trace metals in estuary

An estuary is defined as a zone where seawater is mixed with, and diluted by fresh water (Burton and Liss, 1976). These two types of water have different compositions, thus the mixing result strong physicochemical gradients in estuaries. Metals introduced into an estuary are involved in a number of chemical, biological, and physical processes that will ultimately determine their concentrations in the water column, in the suspended solids and in the sediments. Figure 1-2 illustrated trace metals cycling in a lake. The most important removal process of metal ions from the water column is settling in association with particulate material. The efficiency of this process depends on the composition of the particulate material and on the binding process (adsorption to surfaces, uptake by biota, precipitation of solid phases), as well as on the speciation of the metal ion in solution. Both biogenic organic particles (algae, biological debris) and inorganic particles (e.g. manganese and iron oxyhydroxides) may contribute to the biding and transport of metal ions.

Sedimentation is a dominant process that removed metal ions to sediments; thus it acts as a sink for trace elements in lakes. It also acts as a source of dissolved trace elements, which are released from sediment into water body. Near to the sediment-water interface, anoxic conditions may occur which iron and manganese oxides undergo reduction and dissolution. Trace metals are affected by these processes in different ways (interactions with iron and manganese oxides, precipitation, and complexation with sulfide which may be formed).

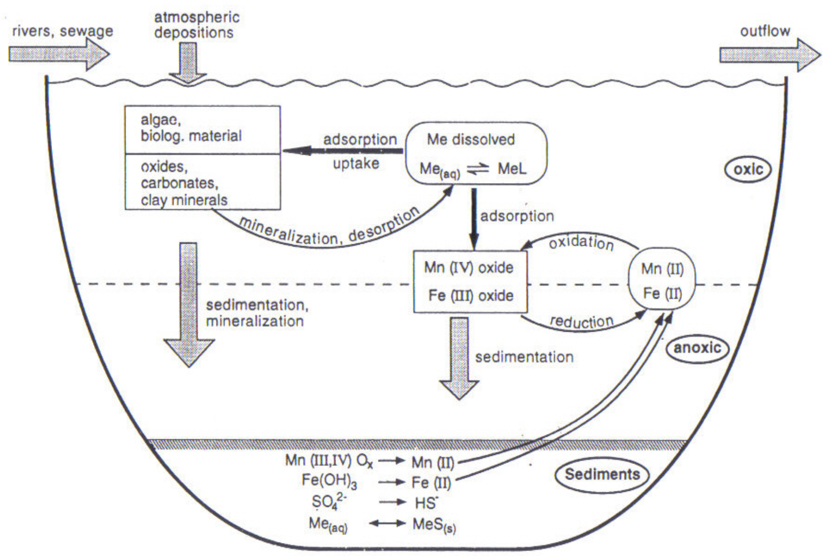

Figure 1- 2 Schematic representation of the cycling of trace elements in a lake
Source: (Sigg, 1994)

1.3 Flux measurement

1.3.1 Diffusive flux

Flux is defined as the rate that fluid, chemicals, particles, or energy flows through a surface. Diffusive flux was resulted from the concentration gradient at the sediment-water interface. It measured the transportation of metals from pore water to the overlying water. Diffusive flux can be computed by using Fick's first law (Berner, 1980) as showed in the equation (1-1) when the concentration gradient at the sediment-water interface is known and proper correction of the diffusion coefficients is made to simulate sediment tortuosity (Ciceri *et al*., 1992; Cheevaporn *et al*., 1995; Alongi *et al*., 1996; Chaichana, 2001, Warnken *et a*l., 2001; Monbet, 2004).

$$J = -\phi D_s \frac{dC}{dz} z{=}o \qquad (1\text{-}1)$$

Where

J	is the diffusive flux (mol cm^{-2} h^{-1})
ϕ	is the porosity of the surface sediments
D_s	is the sediment diffusion coefficient (cm^2 s^{-1})
$\frac{dC}{dz}$	is the concentration gradient occurring over a distance

The concentration gradient between near bottom water and pore water were measured. A number of methods have been used to collect pore water, including: squeezing undisturbed sediment cored under inert atmosphere and controlled temperature, using in situ dialysers inserted into the sediments and centrifugation of sediment cores at vary high speed under inert atmosphere and controlled temperature. Concentration of metals in pore water from different sites is presented in Table A-1 in Appendix A.

The studies of metals diffusive fluxes from various estuaries were presented in Table A-2 in Appendix A. The diffusive fluxes of metals in Thailand estuary were reported by Cheevaporn *et al.,* (1995). In Bang Pakong River Estuary, the diffusive fluxes of metals across the sediment-water interface were in the order of Cu > Zn> Pb> Ni.

1.3.2 Benthic flux

Benthic flux is the transport of dissolved chemical species across the sediment-water interface at the bottom of aquatic systems. Processes responsible for the benthic flux are the upward flow of pore water caused by hydrostatic pressure, molecular diffusion due to concentration gradients (e.g. concentrations in pore waters are generally higher than in overlying waters), mixing of sediment and water at the interface due to bioturbation and water turbulence (Petersen *et al*., 1997). The benthic fluxes effect element concentration in both pore water and overlying bottom water; thus they are important processes of the aquatic biogeochemical cycles of many elements (Rivera Duarte and Flegal, 1994; Riedel *et al*., 1997). Benthic fluxes of Cd, Cu, Pb, Fe and Mn from different sites are presented in Table A-3 in Appendix A.

Benthic flux was calculated by using equation (1-2) (Ciceri *et al*., 1992, William *et al*., 1998).

$$Js = (C_{t1} - C_{t0})\ h\ \Delta t^{-1} \tag{1-2}$$

Where

J_s is benthic fluxes

C_{t0} is concentration of metal in the water at the beginning of experiment

C_{t1} is concentration of metal at hour

Δt is time interval $= t_1 - t_0$

h is the height of the water column inside the benthic chamber

However, the calculation of fluxes on the basis of point-to-point variations contributes to an apparent high variability of the results. This calculation might work for data with a very low experimental error but is unsuitable for trace components subject to a relatively high uncertainty. Thus the calculation of benthic flux for trace metals is purposed by Turetta *et al.* (2005) as showed in equation (1-3).

$$F_b = R/S \tag{1-3}$$

Where

F_b is the mean benthic flux during the experiment,

R is the slope of the regression line of concentration changes in pmol/h

S is the sediment surface covered by the chamber.

This equation is used in order to reduce the effect of the uncertainty of the data; the mean variation of amount of trace elements was obtained from the slope of the regression line for the plot of concentration versus hours. In this study, the above equation is used in the benthic flux calculation.

1.3.3 Benthic chamber

A benthic chamber is a device that is placed on the sediment, enclosing a known area of the sediment surface together with a known volume of ambient overlying bottom water. Various materials for assembly benthic chamber are presented in Table A-4 in Appendix A. The plastic materials such as polycarbonate (Warnken *et al*., 2001), PVC and polymethacrylaten (plexiglass) (Ciceri *et al*., 1992, Zago *et al*., 2000) are suitable materials for trace metals study which are often designed as cylindrical chamber. One important factor is to maintain hydrodynamic conditions in the chamber as natural as possible. Thus the water body in the chambers should be gently stirred and should not disturb sediment surface. In order to calculate fluxes, the volume of water in the chamber must be known. It is calculated from dilution factor of inert marker such as cesium chloride, cesium bromide or strontium chloride which was added a known concentration into the chamber after lid closure (Colbert *et al*., 2001, Berelson *et al.,* 1986). Prior to deployment chamber must be thoroughly cleaned (with e.g. distilled acid and distilled water) and then soaked either in ambient seawater (if possible) of distilled water for a couple of days before use. To ensure that there is no chemical exchange between the chamber walls and the water they enclose. Any substances leaching out of the chamber wall may either contaminate the fluxes of interfere with the chemical measurements.

1.4 Metal Analysis

Metal analysis was performed by either Flame Atomic Absorption Spectrophotometer (FAAS) or Graphite Furnace Atomic Absorption Spectrophotometer (GFAAS) depends on metal concentration. The direct determination of trace metals in estuarine water was difficult to perform due to the low concentration of metals and salt content in the samples. In many instances, it has been necessary to use a preconcentration method prior to analysis. Most widely used methods are solvent extraction (Sirinawin *et al.,* 1998, Nyuyen *et al*., 2005), solid-phase extraction (Tuzen and Soylak, 2006) and precipitation (Esteban *et al*., 1999). Solvent extraction techniques have been widely used due to their favorable concentration factors, removal of matrix salts and matrix normalization effects besides their simplicity, speed, low cost and ease in manipulation. This method uses chelating agent in a non-aqueous phase: e.g. diethyl ammoniumdiethyldithio-carbamate (DDDC), ammoniumpyrrolidindithiocarbamate (APDC) or a mixture of the two (Kinrade and Van Loon, 1974). Chloroform is one of a commonly used organic solvent because of its good extractability (Bruland and Franks, 1979).

1.5 Study site: The Outer Songkhla Lake

Songkhla Lake is the largest lagoonal water in Thailand and Southeast Asia. This body of water is surrounded by three provinces: Songkhla, Phatthalung and Nakhon Si Thammarat. It is located in Southern Thailand between latitudes 7°08′ and 7°50′ N, and longitudes 100°07′ and 100°37′ E. The Songkhla Lake was divided into four parts; Thale Noi, Inner Lake, Middle Lake and Outer Lake (Thale Sap Songkla). The Outer Lake is located in the lower part of Songkhla Lake and covers an area of 176 km^2 with approximate depth of 1.5 meter, except the area around the mouth of the lake which is about 12-14 meter deep. This part of lake extends from Tombon Pak Ro, Singha Nakhon district and Songkhla city (Figure 1-1). The Outer Lake is connected to the Gulf of Thailand via narrow channel where tidal current plays an important role in controlling salinity gradients. It is thus estuarine in character. The salinity is also influenced by the volume of rainfall. During the dry season (April to August), the average salinity was more than 30 psu while during wet season (September to January) it decreased to less than 20 psu. Some physico-chemical conditions and trace metals studies in the Outer Lake were shown in Table A-5 and Table A-6 in Appendix A, respectively. Source of pollutants to the lake are unsanitary drainage from the Songkla urban area, pollutant from boats and fish waste from Songkhla harbor, near shore drainage, municipal waste from HatYai city, and wastes from rubber, parawood and seafood processing industries which were discharged into the U-Tapao Canal (Environmental Department, Division 12, 2000). The data of trace metal studies in 2004 show no indication of anthropogenic contamination of trace metals in both water bodies and surface sediment in the Outer

Lake (Kongtong and Nakinchart personal communication). However, the study of behavior of trace metals in sediment- water interface is of interest.

1.6 Research Objectives

The objectives of this study were (i) to investigate the effect of oxygen and salinity to metal concentrations in overlying water in laboratory and (ii) estimate fluxes of cadmium, copper and lead in the Outer Songkhla Lake using the lab-built benthic chambers.

1.7 Anticipation Outcome

The information of metals fluxes from this study provides more understanding of mobilization processes and geochemical behaviors of these metals at the sediment-water interface in the Outer Songkhla Lake.