CHAPTER 1

INTRODUCTION

1.1   Characteristic of Natural Waters

The hydrosphere is the biggest area of the earth's surface of which extends over 71% of the surface whereas over 97% is the water in the ocean and only less than 3% is inland waters. Water is the essence of life on earth and totally dominates the chemical composition of all organisms (Wetzel, 2001). Natural waters can be categories into freshwater, estuarine or brackish water and seawater.

1.1.1 Fresh water

All freshwater ultimately comes from precipitation of atmospheric water vapor, reaching inland lakes, rivers, and groundwater bodies directly, or after melting of snow or ice. The ionic composition of fresh water is dominated by diluted solutions of alkali and alkaline earth compounds, particularly bicarbonates, carbonates, sulfates and chlorides. The amount of silicic acid, which occurred largely in undissociated form, are usually small but occasionally are significant, particularly in hard water lakes and streams. The major cations are Ca^{2+}, Mg^{2+}, Na^+ and K^+; major anions are HCO_3^-, CO_3^{2-}, SO_4^{2-} and Cl^-. Average concentrations of major dissolved constituents in river water are showed in Table 1-1.

Table 1- 1   Major dissolved constituent in global rivers and in sea water

	river	seawater
constituents	Concentration(mg/L)	Concentration(mg/L)
Calcium	15	412
Potassium	2.3	399
Magnesium	4.1	1,294
Sodium	6.3	10,770
Iron	0.7	<0.01
Chloride	7.8	19,340
Sulphate	11.2	2,712
Bicarbonate	58.4	140
Silicon	13.1	<0.1 to >10

Source : Burton and Liss, 1976

1.1.2 Estuarine water

Estuary is defined as follows: "An estuary is an inlet of the sea reaching into a river valley as far as the upper limit of tidal rise, usually being divisible into three sectors: (a) a upper marine or lower estuary, in free connection with the open sea; (b) a middle estuary, subject to strong salt and fresh water mixing; and (c) an upper or fluvial estuary, characterized by fresh water but subject to daily tidal action" (Fairbridge, 1980). Conditions in an estuary are always changing, and this non-stability or variability is one of the most important features of estuaries. The variation of salinity of estuarine water depends on the tide and the strength of the inflowing river (Burton and Liss, 1976). The increase of ionic strength from approximately 0 to 0.7 M, together with the changes of composition, causes removal of some constituents by flocculation and change of dissolved chemical forms of others (Dyrssen and Wedborg, 1980).

1.1.3 Seawater

In contrast to most natural waters which chemical compositions vary greatly, the chemical composition of seawater is remarkably similar from sea surface to sea floor and from ocean to ocean. Seawater contains large numbers of electrically charged particles, or ions. These may be positively or negatively charged. As a result the physical chemistry of seawater is extremely complex. The most abundant ions in seawater (Table 1-1), such as chloride, sodium, calcium, potassium, magnesium, and sulfate, are present in constant proportions because their concentrations are largely controlled by physical processess; the addition or removal of water. These salts are termed conservative ions. The rest of the substances in seawater are nonconservative because the concentrations are altered by chemical reactions that occur in the ocean and sediment.

1.2 Trace Elements in Natural Waters

1.2.1 River water

Trace metals are transported to the rivers or streams by different paths; overland flow and ground water flow. The path by which water reaches a stream depends upon climate, geology, topography, soil, vegetation and landuse. Trace metals enter rivers from natural sources which include weathering and atmospheric input, and from anthropogenic sources. The weathering of soil and minerals involves both physical and chemical processes. Physical processes break parent rocks into small fragments, thus increasing the surface area that can undergo chemical weathering while chemical weathering processes involve hydrolytic reactions resulting from acidification (rainwater which is in equilibrium with atmospheric carbon dioxide gives a pH of 5.6). In ground water, the weathering of bedrock is the major source of trace metals and the transportation of inorganic colloids through sand and gravel has the potential to transport adsorbed compound. Surface runoff contains high concentrations of suspended particulate matter (SPM) and colloidal matter while ground water has a relatively constant solute concentration due to its longer residence time. The residence time of river is in the order of 2 weeks (Freeze and Cherry, 1979). The contribution of dissolved species to the total amount of each element will differ between rivers (Martin *et al*., 1993; Shafer, *et al.,* 1997) and may vary drastically over the seasons (Shafer, *et al.,* 1997). Dissolved and particulate trace metals concentrations in some rivers are presented in Table 1-2.

Table 1- 2   Dissolved (ng/L) and particulate (mg/L) trace metals concentrations in river waters

Area	Cd		Cu		Pb		Zn		Ref.
	Diss	Part	Diss	Part	Diss	Part	Diss	Part	
Lena River (Russia)	5.6	-	616	37.2	16.5	21.6	347	5.9	Martin *et al.*(1993)
Milwaukee River (U.S.A.)	4.2	0.014	660	0.7	56	0.7	340	2.3	Shafer *et al.*(1997)
Wolf River (U.S.A.)	3.2	0.001	200	0.09	53	30	240	0.2	Shafer *et al.*(1997)
Tigris River (Turkey)	-	-	10	-	-	-	40	-	Gumgum *et al.*(1994)

1.2.2   Estuarine water

Estuaries tend to act as sinks for heavy metals from rivers and the atmosphere where there is time for chemical and physical processes of trace metals to occur before precipitated into sediment or swept out to sea. The nature of estuary can influence the level of trace metal retention. An important process for trace elements in estuaries is the mixing of the fluvial and marine waters and sediments. Stable particulate suspensions in fresh water become destabilized in saline water, leading to flocculation. This depends on flow rate of the water and concentration of the particulate materials (Fergusson, 1991).

The chemical behavior of a trace metal during its transport within the estuary is determined to a large extent by its chemical form in which it is transported by the river: (1) in solution as inorganic ion and both inorganic and organic complexes, (2) adsorbed onto surfaces, (3) in solid organic particles, (4) in coating on detrital particles after co-precipitation with and sorbing onto mainly iron and manganese oxides, (5) in lattice positions of detrital crystalline material, and (6) precipitated as pure phases, possible on detrital particles (Duinker, 1980). Thus, trace metal fractions are available in dissolved and adsorbed forms. The concentration of trace metals in estuary vary considerably, from place to place, depending on the inputs. Trace metal concentration in various estuaries presented in Table 1-3.

Table 1- 3   Average concentrations (µg/L)of dissolved and particulate trace metals in some estuaries

Area	Cd		Cu		Pb		Zn		Ref.
	Diss	Part	Diss	Part	Diss	Part	Diss	Part	
Outer Songkhla Lake (Thailand)	0.008± 0.007	0.002± 0.001	0.358± 0.126	0.244± 0.027	0.022± 0.045	0.778± 0.444	0.43± 0.32	1.28± 0.63	Sirinawin *et al.* (1998)
Outer Songkhla Lake (Thailand)	0.035		0.067		0.226		-		Thompolkrang *et al.* (1995)
Tay Estuary (Scotland)	0.007	-	0.6	-	0.08	-	0.6	-	Owen and Ball (1997)
Changjiang Estuary (China)	0.016± 0.012	0.277± 0.265	1.451± 0.112	68.9± 36.1	0.557± 0.064	44.2± 25.6	1.43± 0.19	137.0± 78.9	Wang *and Liu* (2003)
Scheldt Estuary (Belgium)	0.09	-	1.4	-	0.09	-	4.5	-	Baeyens *et al.* (1998a, 1998b)

The Changjiang estuary (China), the rapid removal of dissolved Fe occurs at very low salinity due to the salt induce coagulation of river-borne colloids. Dissolved Zn shows removal behavior in the low salinity region and non-conservative excess at intermediate and high salinities during the Changjiang estuarine mixing, implying that flocculation at low salinities and deflocculation and desorption process at high salinities occurred separately. Dissolved Cu and Ni have similar distribution. Their concentrations increase at low salinities and then decrease at middle to high salinities, showing non conservative excess behavior owing to desorption reactions. The concentrations of Co and Pb decrease continually with increasing salinity, a non-conservative characteristic of trace metals during estuarine mixing. The removals of both Pb and Co are relatively intense at low salinities compared to intermediate and high salinities. The concentration of dissolved Cd increases linearly with the salinity increasing and the conservative behavior was showed (Wang and Liu, 2003).

In Songkhla lake estuary, Sirinawin *et al.* (1998) reported a characteristic "U" shaped distribution of dissolved and suspended matter of Cu, Ni, Pb, Zn, Fe and Mn with maxima at both low and high salinity, and a settling region in the main body of the Lake. The maxima in suspended concentration at low and high salinities appear to be closely related to the morphology of Songkhla Lake where the constrictions in the narrow flow channel can be expected to increase the bottom friction and thus lead to increase suspension of particulate material, with the result that the estuary has unusual suspended solid distribution with two maxima. Dissolved Cd is the only metal which showed a conservative behavior. The concentration of Cd increased with increasing salinity.

In temperate estuary, the Humber estuary (UK), the behavior of dissolved Cd and Cu exhibited conservatively. The partitioning effect of Cd is sufficiently prominent that Cd in estuarine environments is dominated by the influence of chloride upon dissolved phase complexation. The behavior of Cu seems to be controlled by binding to dissolved phase organic ligands, serve to stabilize Cu in the dissolved phase (Comber *et al.*, 1995).

In Galveston Bay, Texas (USA), Cd, Cu, Ni, Pb and Zn showed non-conservative mixing behavior with mid-salinity maxima (Tang *et al.*, 2002). The non-

conservative distribution likely results from the interplay between complexation of trace metals to organic ligands which would hinder their removal by particles, in particularly Cu, greater than 99.9% of dissolved fraction was present in the form of organic complex (Tang *et al*., 2002). Non-conservative behaviors of Cd, Cu, Pb, Mn, Ni and Zn in Tay estuary (Scotland) were also reported by Owens and Balls (1997). The interactions with biogenic and detrital particulate phases are important in controlling dissolved trace metals concentrations. Removal of dissolved metals was observed in the turbidity maximum zone. This could be accounted for adsorption onto suspended particulate matter (Owens and Balls, 1997).

The laboratory experiments of the behavior of Cd, Cu, Fe, Mn, and Zn in the mixing of Aber-Wrac'h (France) river water and seawater were conducted by Roux *et al*. (1998). Copper had a conservative behavior in both the dissolved and the particulate phase. The affinity for organic matter was well established for dissolved copper as well as for particulate copper. Manganese and cadmium were non-conservative: A clear enrichment of the dissolved phase was observed at low salinities (<7.5). These metals were desorbed in inorganic form from the particulate phase and for a large part from the carbonates fraction of the SPM. Iron was partly removed from the dissolved phase during the mixing, probably because of organic matter flocculation. Particulate iron was conservative (Roux *et al*., 1998).

1.2.3 Seawater

Metals are introduced into seawater by river runoff, winds, hydrothermal venting, diffusion from sediments, and anthropogenic activities. Rivers are a major source of particulate and dissolved metals, both of which are mobilized during the weathering of granitic and basaltic crust. Some of the particulate trace metals are present as cations adsorbed onto the surfaces of clay minerals. The increase in ionic strength that occurs when river water meets seawater leads to the desorption of some of these trace metals. The increase in ionic strength and pH also causes these resolubilized metals to precipitate as oxyhydroxides and organometallic colloids. The average concentration and speciation of the elements in sea water (salinity 35 psu) are showed in Table 1-4.

Table 1- 4   The species, concentration ranges, and average concentration of the elements in seawater (salinity 35 psu)

Element	Main species in oxygenated seawater	Range concentration nmol/kg	Average concentration nmol/kg
Cd	$CdCl_2^0$	0.001-1.1	0.7
Cu	$Cu^{2+}, CuCO_3^0, CuOH^+$	0.5-6	4
Pb	$PbCO_3^0, Pb(CO_3)_2^{2-}, PbCl^+$	0.005-0.2	0.01
Zn	$Zn^{2+}, ZnOH^+, ZnCO_3^{0-}, ZnCl^+$	0.05-9	6
Al	$Al(OH)_4^-, Al(OH)_3^0$	5-40	20
Fe	$Fe(OH)_3^0$	0.1-2.5	1
Mn	$Mn^{2+}, MnCl^+$	0.2-3	0.5

Source: Chester (1990)

1.3   Classification of Metals

Metal ions are classified into three categories based on covalent interaction. They are A-type (hard), B-type (soft) and borderline type (between A and B types).

Metals in class A tend to be ionized in solution, which result in cations with a closed shell configuration and an inert gas structure. Class A metals include K^+, Li^+, Na^+, Ba^{2+}, Ca^{2+}, Mg^{2+}, and Al^{3+}. These cations are nonpolarizable, highly stable, and, in general, formed weak complexes in solution via electrostatic bonding. The ligand-binding preferences of class A metals for the following anions decrease in the order F>O>P>N>S. The preferable complexes are fluoride and ligands having oxygen as the donor atom. No sulfides (precipitates of complexes) are formed complexes by these ions in aqueous solution. Chloro- or iodo-complexes are weak and it occurs most readily in acid solutions under the OH⁻ competition (Mason. and Jenkins, 1995).

The borderline metals show ligand-binding characteristics that are intermediate to those of group A and B metals. Turner *et al. (*1981) classified borderline group based upon binding strength to fluoride and chloride complexes which is in the order as; $Fe^{3+}<Fe^{2+}=Cu^{2+}<Mn^{2+}<Zn^{2+}<Pb^{2+}<Co^{2+}=Ni^{2+}<Cu^+<Cd^{2+}$.

Metals to the left of the sequence form stronger fluoro-complexes than chloro complexes. Those to the right have a stronger B class character.

Metals in class B tend to form covalent bonds and show a reversed preference of binding to the class A metals (S>I>Br>Cl=N>P>O>F). Metals within this class include Ag^+, Au^+, Tl^+, Hg^{2+}, Bi^{3+}, Tl^{3+}. They form stable I^- or Cl^- complexes than F^- complexes and form insoluble sulfide.

1.4   Distribution Coefficient (K_D) of Trace Metal

The interaction of trace elements with the surfaces of solid particles is important in regulating the solute concentration in natural water. Solid particles in natural water include oxide of aluminum, iron and silicon, silicate minerals and biological debris. The interactions of cations and anions with the particle surfaces can be explained by electrostatic interactions, complexation, adsorption reaction and coordination reactions onto the particle surface (Stumm, 1987).

The distribution coefficient of element between the dissolved and solid phases gives a better picture than the fraction of metal ions in solution since it is independent of the concentration of suspended solids in water. It depends on pH and on the grain size of the particles. The distribution coefficient is expressed by the term K_d and it is of the following form:

$$K_d \quad = \quad C_s/ C_w$$

where C_s is the metal concentration in solid particle (w/w).
C_w is the metal concentration in dissolved form (w/v).

In tropical estuary, Songkhla Lake estuary (Thailand), the K_d profiles of trace metals revealed different behaviors of metals which were classified into three groups: firstly Cu, Pb, Zn and Fe, with little coherent change in partitioning with salinity. Secondly Cd, which is conservative in dissolved phase; and finally Mn, Co, and Ni, which showed a minimum in partition coefficient in the mid-salinity region.

It is indicated that Cu, Pb and Zn are associated with suspended Fe oxides while Co and Ni are adsorbed to suspended Mn oxides (Sirinawin *et al*., 1998).

In Changjiang estuary (China), the K_d values of heavy metals are mainly influence by salinity and particle concentrations. The K_d of Fe, Ni and Cd change considerably with increasing salinity, reflecting the removal of dissolved iron and desorption of Ni and Cd (Wang and Liu, 2003).

In temperate estuary, Galveston Bay (USA), the partitioning of trace metals between dissolved and particulate fractions showed the log K_d values for Cu and Ni close to 4. Both metals were shown to be organically bound. The relatively high K_d values for Pb were likely due to its high affinity for clays, metal oxides and sulfides, and its intermediate affinity for organic matter. Values of K_d for Zn and Cd were between those for the strongly organically bound trace metals (Ni and Cu) and those for surface-reactive elements such as Pb, Ag and Hg (Tang *et al*., 2002).

In the Thame estuary (UK), the distribution coefficients of Mn and Pb exhibit large differences between the inner estuary and the plume region. For all the metals (Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn) except Cu and Cd the distribution coefficient is about ten times lower in the inner than in the outer estuary (Burton *et al.,* 1993)

1.5   Songkhla Lake System

Songkla Lake is a tropical estuarine lagoon system with a unique characteristic. It is one of the largest lakes in Southeast Asia, located in Songkla, Pattalung and Nakhon Si Thammarrat Provinces, between latitudes 7° 08′ N and 7° 50′ N and between latitudes 100° 07′ E and 100° 37′ E. The total area is 1,042 km^2 and its average depth is 2 metres. It is comprised of Thale Noi (TLN), Inner Lake, Middle lake and Outer Lake, from north to south, which is inter-connected by narrow channels. The Outer Lake connected to the Gulf of Thailand (seaward) at its southeastern end through a narrow channel 420m wide and 9.5m deep. A gradient of salinity exists, between the freshwater of TLN and brackish water of the Outer Lake. The Inner Lake and the Middle Lake approach freshwater condition during the rainy season (October - January), but they are influenced by the invasion of seawater in

other month. Water quality in 2004 was reported by Buakaew (2005) as oxidizable organic carbons 0.66-6.23%, total carbon 0.76-7.94%, total nitrogen 0.15-0.71%, total sulfur 0.14-1.81% and total phosphorus 0.013-0.021%. The Outer Lake is known for its production of fish, shrimp and crabs, and is also intensively utilized for the aquaculture of seabass *(Lates calcarifer).* A severe eutrophication problem in the Middle Lake was reported in 2002 (Sompongchaiyakul *et al.,* 2004). However, the complete and rapid turnover of water in the rainy season seems to prevent severe problems. The rate of sedimentation in Songkhla Lake ranged between 5.0-6.9mm/yr (Songkhla Lake Basin Master Plan, 2005).

Previous study of trace metals behaviors in the Outer Lake was performed by Sirinawin *et al.* (1998). The water samples were collected in 1987. It was found that cadmium is conservative in dissolved phase; copper, lead and zinc were associated with iron while cobalt and nickel were associated with manganese.

This study is the first investigation of the concentration and distribution of trace metals in the whole Songkhla Lake System which comprises of different water characteristics; fresh water, estuarine water and saline water in both wet and dry seasons. The behaviors of cadmium (Cd), copper (Cu), lead (Pb), zinc (Zn), aluminium (Al), iron (Fe) and manganese (Mn) were studied in order to gain more understanding of their geochemistry in the lake.
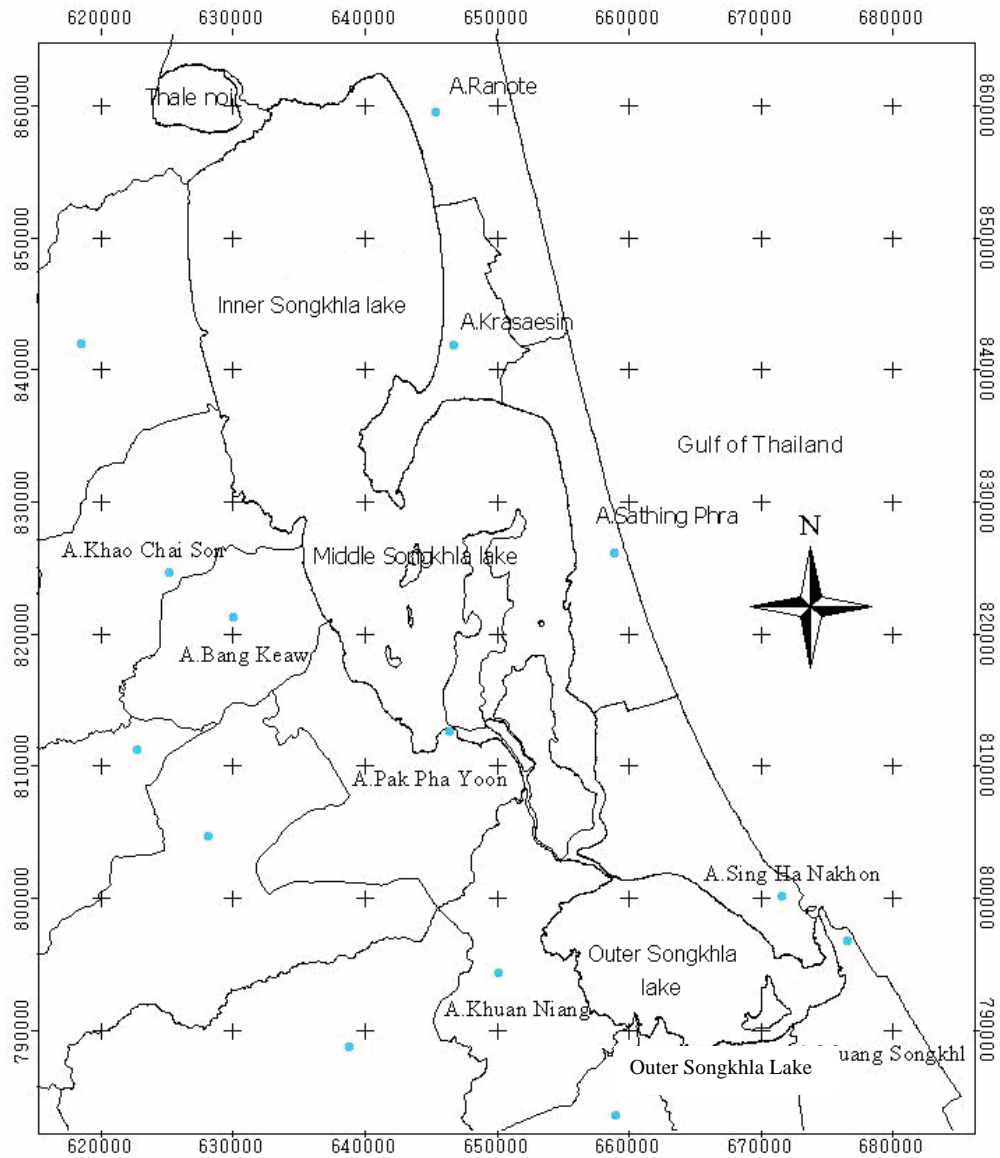
Figure 1 - 1 Map of Songkhla Lake System

1.6   Trace Metals Determination

1.6.1 Analytical Methods

There are several analytical techniques being used for determination of trace metals such as graphite furnace atomic absorption spectrophotometry (GFAAS), flame Atomic absorption spectrophotometry (FAAS), inductively coupled-plasma atomic emission spectrometry (ICP-AES), inductively coupled-plasma mass spectrometry (ICP-MS), anodic stripping voltammetry (ASV) and differential pulse anodic stripping voltammetry (DPASV).

1.6.1.1   Graphite Furnace Atomic Absorption Spectroscopy (GFAAS)

In atomic absorption spectrometry, GFAAS is widely used for determination of trace metals in terms of total metal concentration. Generally, GFAAS provides enhanced sensitivity because the entire sample is atomized in a short period and the average residence time of the atoms in the optical path is a second or more. In GFAAS, a few microlitres of the sample are first evaporated at a low temperature and ashed at a higher temperature in an electrically heated graphite tube or cup. After ashing, the current is rapidly increased to several hundred amperes, which cause the temperature to rise to approximately $2,000^{o}C$ to $3,000^{o}C$; atomization of the sample occurs in a period of few milliseconds to seconds. The absorption of the atomized particles is then measured in the region immediately above the heated surface (Strobel and Heineman, 1989; Skoog and Leary, 1992).

The advantage of GFAAS usually offers high sensitivity for small volumes of sample. Typically, a wide range of sample volumes is between 0.5 μL and 99 μL can be employed. Absolute detection limits typically lie in the range of 10^{-10} to 10^{-13} g of analyte with an injection volume between 0.5 μL to 10 μL (Skoog and Leary, 1992). GFAAS has been applied for the determination of trace metals in natural waters (Sturgeon *et al.,* 1982; Landing *et al.,* 1986; Chan and Huang, 2000; Anthemidis *et al.,* 2001; Comber *et al.,* 1995; Lui and Huang, 1995; Pesavento *et al.,* 1999; Cabon, 2005).

1.6.1.2 Inductively Coupled-Plasma Atomic Emission Spectrometry (ICP-AES)

Inductively coupled-plasma (ICP) is an ion source operated at atmospheric pressure. By the time the analyte atoms and ions reach the observation point in the plasma, they have spent about 2 ms in the plasma at temperatures ranging from 6000 to 8000 K. These times and temperatures are two to three times greater than those attainable in the hottest combustion flames (acetylene/nitrous oxide). As a consequence, desolvation and vaporization are essentially complete, and the atomization efficiency is quite high. Therefore, there is less chemical interference in ICPS than in combustion flames. An ionization interference effects are small non existent because the large concentration of electrons from the ionization of argon maintains a more-or-less constant electron concentration in the plasma.

Several other advantages are associated with the ICP when compared with flames and other plasma sources. Atomization occurs in a chemically inert environment, in contrast to flames, where the environment is violent and highly reactive. In addition, the temperature cross-section of the plasma is relatively uniform. The plasma also has a rather thin optical path length, which minimizes self-absorption. One significant disadvantage of the ICP is that it is not very tolerant of organic solvents. Carbon deposits tend to build up on the quartz tube, which can lead to cross-contamination and clogging (Skoog, West, Holler and Crouch, 2004).

1.6.1.3 Voltammetry (ASV and DPASV)

In anodic stripping voltammetry (ASV), the metal is first cathodically reduced at a suitable deposition potential on a hanging mercury drop or film electrode and is accumulated on its mercury amalgam. A subsequent oxidative stripping step (reverse polarography) permits one to measure the anodic current during the oxidative step. Its peak current resulting from the integral of current versus time relates to the metal concentration (Copeland and Skogerbore, 1974; Wang, 1982).

Differential pulse anodic stripping voltammetry (DPASV) technique is similar to the conventional ASV technique. The difference is that the metal ions are stripped from the electrode by a conventional positive-going linear voltage ramp with

voltage pulses and constant amplitudes, which are superimposed on a linear potential ramp. The differential current is obtained by subtracting the current measured before the end of the pulse life. Due to an increased signal-to-noise ratio, the sensitivity of DPASV is greater than for conventional ASV (Florence, 1986). Therefore, DPASV is employed for more dilute solutions rather than conventional ASV and even for highly acidic media (Laxen and Harrison 1983; Florence, 1986; Bott, 1995).

1.6.2   Pre-concentration Method

The pre-concentration and separation procedure is usually incorporated into the sample preparation in order to solve the problem of low concentration of heavy metals and the present of interfering components in environmental samples. Common pre-concentration and separation methods such as solvent extraction, coprecipitation, and methods based on ion exchange resin or sorbents in packed column were employed (Skoog, West, Holler and Crouch, 2004)

1.6.2.1   Solvent Extraction

Solvent extraction techniques have been widely used for the pre-concentration of trace metals from water sample as a preliminary step in the determination by using analytical techniques. The process of solvent extraction, the metals ions that contain in aqueous phase are extracted with chelating ligands (or complexing agent) into organic solvent. This is because the coordinated water molecules of metal ions are replaced with the ligand groups, so as to produce complexes, chelate complexes, which are essentially non-polar and usually soluble in organic solvents. In forming chelate complex, the central metal ion coordinates with a polyfunctional organic base to form one or more stable six-membered ring structures.

A chelating ligand must be anionic in nature so that it is capable of neutralizing the positive charges on metal cations. It must also contain nitrogen, oxygen or sulphur atoms which are capable of donating electrons into vacant orbitals of metals atoms (Watana, 1989). The complexing ligands have been most frequently used such as 4-morpholine dithiocarbamate (Todorovic, 2002), ammonium pyrolidine dithiocarbamate(APDC), diethylammonium diethyldithiocarbamate (DDDC) (Bajo

and Wyttenbach, 1979) or the mixture between APDC and DDDC (Danielsson *et al.,*1982; Kinrade and Van loon, 1974; Mackey *et al.,*1997; Sirinawin *et al.,* 1998). The combination of these chelating reagents worked well for the extraction of a variety of metals over a fairly wide pH range (Bruland and Franks, 1979).

The organic solvent used in extracting the metal complexes formed must show a number of desirable characteristics: extract the desired metal-chelates, be immisible with the aqueous solution, not tend to form emulsions, have good burning characteristics, enhance rather than suppress the atomic absorption sensitivity as compared to the metal in water and low toxicity (Kinrade and Van Loon, 1974). Several organic solvents are used in chelate extraction such as freon-113 (Mackey *et al.,* 1997; Sirinawin *et al.,* 1998), methylisobuthyl ketone (MIBK) (Kinrade and Van Loon, 1974 , Danielsson *et al,* 1978), chloroform (Todorovic, 2002) and carbon tetrachloride (CCl_4) (Chakraborti, 1987). MIBK and chloroform are the most or common organic solvents which are used together with APDC because they show quite good extractability. The great advantages of solvent extraction techniques are their favorable concentration factors, removal of matrix salts and matrix normalization effects besides their simplicity, speed, low cost and ease in manipulation.

1.6.2.2 Coprecipitation

Coprecipitation techniques have been favored for the concentration of trace metals from natural water (Edward and Edmond, 1977; Atsuya, 1991). In general, coprecipitation can occur in two ways. Firstly, the coprecipitated element may be incorporated into the lattice of the precipitate as a solid solution. Because of the requirement for mixed crystal formation, these types of coprecipitation tend to be specific in its action, and its applicability in the concentration of trace elements from seawater is accordingly limited. Secondly, the coprecipitated element may be adsorped onto the surface of a precipitate having a large surface area. Because of its unspecific nature, this technique is commonly used to concentrate trace metals from seawater. The advantage of this technique is a high concentration factor can be achieved. There are a number of drawbacks or limitations such as their separations are lengthy and time consuming, the precipitate are often gelatinous and difficult to

handle, yield monitors are necessary since recoveries are irreproducible (Watana, 1989).

1.6.2.3 Solid Phase Extraction

The principle of solid phase extraction (SPE) is similar to that of liquid-liquid extraction (LLE), involving a partitioning of solutes between two phases. However, instead of two immiscible liquid phases, as in LLE, SPE involves partitioning between a liquid (sample matrix) and a solid (sorbent) phase. This sample treatment technique enables the concentration and purification of analytes from solution by sorption on a solid sorbent. The basic approach involves passing the liquid sample through a column, a cartridge, a tube or a disk containing an adsorbent that retains the analytes. After all of sample has been passed through the sorbent, retained analytes are subsequently recovered upon elution with an appropriate solvent (Camel, 2003). The advantages of SPE methods are reduce consumption of and exposure to solvents, their disposal costs and extraction time. It also allows the achievement of high recoveries, along with possible elevated enrichment factors. In addition, SPE can be interfaced on-line with analytical techniques such as liquid chromatography (LC) or atomic absorption spectrometry (AAS).

In this study, the methods used for determination trace metals in surface water samples are solvent extraction as a pre-concentration method due to its advantages of favorable concentration factors, removal of matrix salts, simplicity, low cost and ease in manipulation, followed by instrumental methods of GFAAS, FAAS and ICP-AES.

1.7 Statistical Data analysis

Besides of the information of metal concentrations in natural water, the understanding of metal behaviors is of importance. Spatial and seasonal trends of metals usually correspond to the source of enrichment and relate to biogeochemical and hydrological conditions in aquatic system. The distribution coefficient of metals, profile distribution and spatial distribution on their own are not sufficiently to distinguish the metal behaviors. Multivariate statistics methods can describe the relationship of metals in water and factors that influence this more precisely.

Multivariate method can analyze the whole data set instead of individual elements and take into account several factors simultaneously. This corresponds better a real situation in water system. Principal Component Analysis (PCA) is a multivariate statistical method and it was applied to analyze the trace metal pattern in various samples. The detail about the computational aspects of PCA can be readily found elsewhere (Johnson and Wichern, 1992). PCA applications in environmental practices are described by many research groups. Shine *et al.,* 1995 applied PCA to estimate spatial and temporal pattern of heavy metal contamination. Winter *et al.,* 2000 applied PCA to investigate the distribution of various types of water level fluctuation pattern. PCA also enables the metal composition in different samples to be compared and provides fingerprints for identifying the origin of pollution (Burns *et al.,* 1997).

PCA is a multivariate statistical analysis converting the variables (analytical species and concentration) in the so-called factors or principal components, i.e. linear combinations of the variables that are themselves not correlated and together explain the total variance of the data. The first factor explains the most variance, the second factor the next variance and so on. It follows that the dimensionality of the original data space can be reduced to a few factors, commonly two or three, retaining almost all the system variance. The PCA allows 'a factor score' for each sample to be calculated. When plotted by factor scores, samples with similar analyte compositions (i.e. scores) will be closer than those with dissimilar compositions. The similarities among samples can shed light about the similarity of metal behavior and the contamination sources (Carlon *et al*., 2001). In this study PCA was applied to identify groups of metal i.e. correlation between the variables and the principal components.

1.8   Objective

The objectives of this study were (i) to present the partitioning of a number of trace metals (Cd, Cu, Pb, Zn, Al, Fe, and Mn) between the dissolved and particulate phases in order to understanding their biogeochemical behaviors; and (ii)

to obtain the extended database on the distribution of trace metals in Songkhla Lake System (Thale Noi, Inner, Middle and Outer Lake).