

# CHAPTER 1

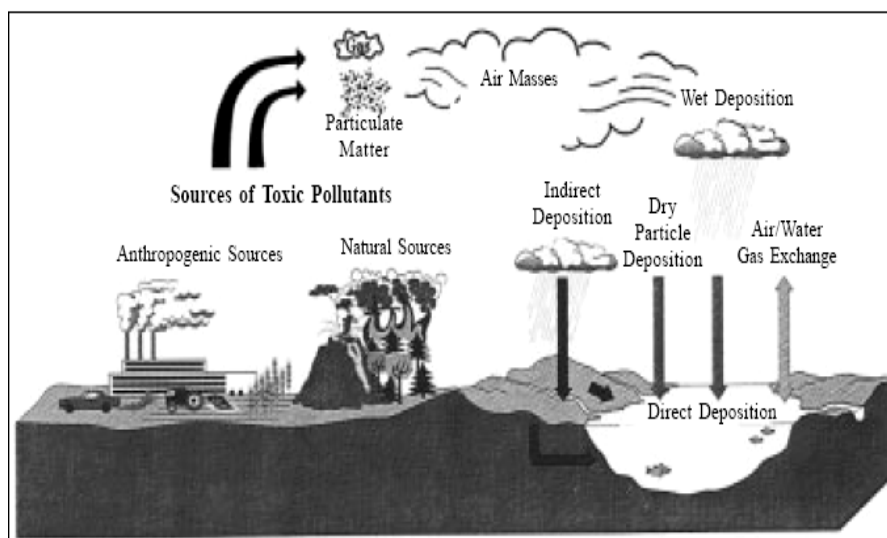
## INTRODUCTION

### 1.1 Introduction

'Heavy metals' is a general collective term applied to the group of metals and metalloids with an atomic density greater than  $6 \text{ g cm}^{-3}$ . Although it is only a loosely defined term it is widely recognized and usually applied to the elements such as Cd, Cr, Cu, Hg, Ni, Pb and Zn which are commonly associated with pollution and toxic problems. Heavy metals occur naturally in rock-forming and ore minerals and so there is a range of normal background concentrations of these metals in soils, sediments, waters and living organisms (Alloway and Ayres, 1993). Heavy metals are most conveniently classified into three groups: essential, non-essential and toxic (Ward, 1995). Heavy metals enter into the environment mainly via three routes: (i) deposition of atmospheric particulates, (ii) disposal of metal enriched sewage sludge and sewage effluents and (iii) by-products from metal mining processes (Shrivastav, 2001).

One important environmental compartment and stage of the biogeochemical cycle of heavy metals is the atmosphere, where the heavy metals occur as aerosols and are bound to dust particles. These metals can be deposited to the surface of water or land via dry fall (dust) or precipitation such as rain, snow and hail (Cheng *et al.*, 1994) by dry and wet deposition constitutes the first stage of accumulation of atmospheric heavy metals. Dry deposition involves four distinct processes: gravitational settling, impaction, turbulent transfer and transfer by Brownian motion. Wet deposition involves two processes: nucleation and within and below cloud scavenging, whereby the wet aerosol particles are collected by falling raindrops (Shrivastav, 2001). Illustrations of atmospheric depositional processes are shown in Figure 1-1. Heavy metals diffuse from many natural sources such as soil dust, sea spray, volcanic and Earth's crust activity (Morselli *et al.*, 2003). And main source of heavy metal emission into the atmosphere are man-made, including industrial activity, coal burning and automobile exhaust. Heavy metals in aerosols

will readily dissolve in the low pH conditions that characterize that are mainly dissolved in rainwater (Roy and Negrel, 2001). Monitoring the concentrations of heavy metals in the atmosphere (aerosols and rain events) provides important information about the sources of these metals and enables budget and flux calculation (Takeda *et al.*, 2000).



**Figure 1-1** Illustration of atmospheric depositional processes (U.S. EPA, 1994)(<http://www.delta-institute.org/publications/airtoxics.pdf>)

Several studies have examined heavy metals in rainwater samples (Takeda *et al.*, 2000). However, there have been few repeated on concentration of heavy metals in rainwater samples collected in Hat Yai City, Southern Thailand.

In this work, we report the concentrations of Cu, Cd and Pb collected in Hat Yai City municipality, Songkhla in South Thailand during the period of 15/10/2004-11/12/2004.

## 1.2 Background

### 1.2.1 Chemical and physical properties of copper, cadmium and lead

#### 1.2.1.1 Copper (Cu)

Copper is a micronutrient which can be deficient in some soils causing severe loss of yield in several crops, especially cereals (Alloway and Ayres, 1993). Copper has two natural isotopes,  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$ , with isotopic abundances of 68.94 % and 31.06 %, respectively. The principal physicochemical properties of copper are summarized in Table 1-1.

**Table 1-1** Summary of some relevant physicochemical properties of copper

Atomic number	29
Electronic configuration	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$
Relative atomic mass	$63.54 \text{ g mol}^{-1}$
Relative density	$8.95 \text{ g cm}^{-3}$ at $20^\circ\text{C}$
Mohs' hardness	3.0
Electrical resistivity	$1.673 \mu\Omega\text{cm}$
Melting point	$1083^\circ\text{C}$
Boiling point	$2595^\circ\text{C}$
Vanderwaals radius	0.128 nm
Ionic radius	0.096 nm (+1); 0.069 nm (+3)
Isotopes	6
Heat of fusion	$205 \text{ KJ kg}^{-1}$
Heat of vaporization	$4810 \text{ KJ kg}^{-1}$
Standard electrode potential	
$\text{Cu}^{2+} + 2\text{e}^- \longrightarrow \text{Cu}$	$E^\circ = 0.337 \text{ V}$
$\text{Cu}^{2+} + \text{e}^- \longrightarrow \text{Cu}^+$	$E^\circ = 0.153 \text{ V}$
$\text{Cu}^+ + \text{e}^- \longrightarrow \text{Cu}$	$E^\circ = 0.52 \text{ V}$
Equilibrium constants <sup>a</sup>	
$\text{Cu}^+ + 2\text{CN}^- \longrightarrow \text{Cu}(\text{CN})_2^-$	$\log \beta_2 = 24$
$\text{Cu}^+ + 3\text{CN}^- \longrightarrow \text{Cu}(\text{CN})_3^-$	$\log \beta_3 = 28.6$
$\text{Cu}^{2+} + 4\text{NH}_3 \longrightarrow \text{Cu}(\text{NH}_3)_4^{2+}$	$\log \beta_4 = 13.3$

<sup>a</sup> values differ considerably among authors.

Source: Cordoba, 1995 and (<http://www.lenntech.com/Periodic-chart-elements/Cu-en.htm>)

As well as in its native states, copper is found naturally as sulphides, oxides and carbonates. The principal materials are chalcopyrite ( $\text{CuFeS}_2$ ), chalcocite ( $\text{Cu}_2\text{S}$ ), bornite ( $\text{Cu}_5\text{FeS}_4$ ), cuprite ( $\text{Cu}_2\text{O}$ ), malachite ( $\text{Cu}_2(\text{CO}_3)(\text{OH})_2$ ) and azurite ( $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$ ).

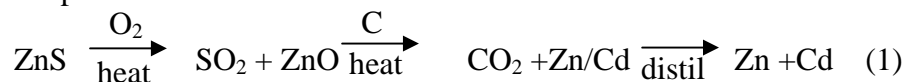
Copper can be found in many kinds of food, in drinking water and in air. Because of that we absorb eminent quantities of copper each day by eating, drinking and breathing. The absorption of copper is necessary, because copper is a trace element that is essential for human health. Although humans can handle proportionally large concentrations of copper, too much copper can still cause eminent health problems. Most copper compounds will settle and be bound to either water sediment or soil particles. Soluble copper compounds form the largest threat to human health. Usually water-soluble copper compounds occur in the environment after release through application in agriculture (<http://www.lenntech.com/Periodic-chart-elements/Cu-en.htm>).

Copper in the atmosphere can be found in dust, and as a consequence, in rain and snow in small quantities. The literature reports data for rain samples ranging from  $0.4$  to  $2.3 \mu\text{g L}^{-1}$  for 'clean' areas, although snow from urban areas has been reported to contain  $15\text{-}70 \mu\text{g L}^{-1}$ . A mean value of about  $2 \text{ ng m}^{-3}$  has been indicated for air of uncontaminated areas. The legal permissible exposure limit in USA was established as  $1 \text{ mg m}^{-3}$  for copper dust and mists and  $0.1 \text{ mg m}^{-3}$  for copper fumes (Cordoba, 1995).

#### **1.2.1.2 Cadmium (Cd)**

Cadmium, a soft, bluish white metal, is quite ductile and more fusible and volatile than zinc. It exists in its natural state in greenockite (77%  $\text{CdS}$ ) and in lead or zinc ores. Its redox potential ( $\text{Cd}^{2+} + 2\text{e}^- \longrightarrow \text{Cd}^0$ ) is  $-0.40 \text{ V}$  vs. NHE. A summary of the physical properties of cadmium are given in Table 1-2 (Chappuis and Pineau, 1995).

Cadmium is obtained as a byproduct from zinc refining (Eqn 1) but the complete removal of all the cadmium from 'bulk' zinc is uneconomical.



Dispersal of zinc therefore leads to dispersal of cadmium (O'Neill, 1993).

**Table 1-2** Some physical properties of cadmium

Atomic number	48
Relative atomic mass	112.41 g mol <sup>-1</sup>
Electro negativity according to Pauling	1.7
Oxidation state	2
Density (20 °C)	8.65 g cm <sup>-3</sup>
Vapor density (air = 1)	3.9
Melting point (S.T.P.)	320.9 °C
Boiling point (S.T.P.)	765 ± 2 °C
Vanderwaals radius	0.154 nm
Ionic radius	0.097 nm (+2)
Isotopes	15
Electronic shell	[Kr] 4d <sup>10</sup> 5s <sup>2</sup>
Energy of first ionization	866 kJ mol <sup>-1</sup>
Standard potential	1622 kJ mol <sup>-1</sup>
Mass fraction in earth's crust	3 × 10 <sup>-3</sup> %
Hydrosphere and atmosphere	

Source: Chappuis and Pineau, 1995 and (<http://www.lenntech.com/Periodic-chart-elements/Cd-en.htm>)

Environmental levels of cadmium can be increased by industrial or waste incineration, fossil fuel combustion, discharge of treated sewage sludge and vehicle exhaust fumes, as well as by natural volcanic emissions. Atmospheric pollution can be monitored by determining cadmium levels in air, dust and plants relative to the distance from emission sources (Chappuis and Pineau, 1995).

### 1.2.1.3 Lead (Pb)

Lead is a bluish-white lustrous metal. It is very soft, highly malleable, ductile, and a relatively poor conductor of electricity. It is very resistant to corrosion but tarnishes upon exposure to air. Lead pipes bearing the insignia of Roman emperors, used as drains from the baths, are still in service. Alloys include pewter

and solder. Tetraethyl lead (PbEt<sub>4</sub>) is still used in some grades of petrol (gasoline) but is being phased out on environmental grounds (<http://www.lenntech.com/Periodic-chart-elements/Pb-en.htm>). The principal physicochemical properties of lead are summarized in Table 1-3.

**Table 1-3** Some physical properties of lead

Atomic number	82
Electronic shell	[Xe] 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>2</sup>
Electro negativity according to Pauling	1.8
Relative atomic mass	207.2 g mol <sup>-1</sup>
Relative density	11.34 g cm <sup>-3</sup> at 20 °C
Melting point (S.T.P.)	327 °C
Boiling point (S.T.P.)	755 °C
Vanderwaals radius	0.154 nm
Ionic radius	0.132 nm (+2);0.084 nm (+4)
Isotopes	13
Energy of first ionization	715.4 kJ mol <sup>-1</sup>
Energy of second ionization	1450.0 kJ mol <sup>-1</sup>
Energy of third ionization	3080.7 kJ mol <sup>-1</sup>
Energy of fourth ionization	4082.3 kJ mol <sup>-1</sup>
Energy of fifth ionization	6608 kJ mol <sup>-1</sup>

Source :(<http://www.lenntech.com/Periodic-chart-elements/Pb-en.htm>)

From U.S. Environmental Protection Agency the Maximum Contaminant Level (MCLs) of Cu, Cd and Pb in drinking waters are shown in Table 1-4.

**Table 1-4** The Maximum Contaminant Level (MCLs) of Cu, Cd and Pb in drinking waters (mg L<sup>-1</sup>)

Metal	MCLs (mg L <sup>-1</sup> )
Copper	1.3
Cadmium	0.005
Lead	0.015

Source: <http://www.epa.gov/safewater/mcl.html>

## **1.2.2 Uses**

### **1.2.2.1 Copper**

Humans widely use copper, it is applied in the industries and in agriculture. Copper sulfate is used as an algicide in ornamental ponds and even in water supply reservoirs which are affected by blooms of toxic blue-green algae. Copper is used widely in houses for piping water (Alloway and Ayres, 1993).

### **1.2.2.2 Cadmium**

Cadmium is used in electroplating (in which it forms a bright corrosion-resistant finish), in plastic stabilizers, in pigments, in solder, and in nickel-cadmium batteries (O'Neill, 1993).

### **1.2.2.3 Lead**

The two major uses of lead are in lead-acid storage batteries, particularly for motor vehicles, and as lead alkyl compounds added to petrol (O'Neill, 1993). Other sources include lead plumbing, glazed pottery, solder used in tin cans, old-pewter, and lead-based paints (Ward, 1993).

## **1.2.3 Health effects**

### **1.2.3.1 Health effects of copper**

Long-term exposure to copper can cause irritation of the nose, mouth and eyes and it causes headache, stomachache, dizziness, vomiting and diarrhea. Intentionally high uptakes of copper may cause liver and kidney damage and even death. Whether copper is carcinogenic has not been determined yet. There are scientific articles that indicate a link between long-term exposure to high concentrations of copper and a decline in intelligence with young adolescents. Whether this should be of concern is a topic for further investigation. Industrial exposure to copper fumes, dusts or mists may result in metal fume fever with atrophic

changes in nasal mucous membranes. Chronic copper poisoning results in Wilson's disease, characterized by a hepatic cirrhosis, brain damage, demyelination, renal disease and copper deposition in the cornea (<http://www.lenntech.com/Periodic-chart-elements/Cu-en.htm>).

### **1.2.3.2 Health effects of cadmium**

Human uptake of cadmium takes place mainly through food. Foodstuffs that are rich in cadmium can greatly increase the cadmium concentration in human bodies. Examples are liver, mushrooms, shellfish, mussels, cocoa powder and dried seaweed.

An exposure to significantly higher cadmium levels occurs when people smoke. Tobacco smoke transports cadmium into the lungs. Blood will transport it through the rest of the body where it can increase effects by potentiating cadmium that is already present from cadmium-rich food.

Other high exposures can occur with people who live near hazardous waste sites or factories that release cadmium into the air and people that work in the metal refinery industry. When people breathe in cadmium it can severely damage the lungs. This may even cause death. Cadmium is first transported to the liver through the blood. There, it is bonded to proteins to form complexes that are transported to the kidneys. Cadmium accumulates in kidneys, where it damages filtering mechanisms.

This causes the excretion of essential proteins and sugars from the body and further kidney damage. It takes a very long time before cadmium that has accumulated in kidneys is excreted from a human body.

Other health effects that can be caused by cadmium include:

- Diarrhea, stomach pains and severe vomiting
- Bone fracture
- Reproductive failure and possibly even infertility
- Damage to the central nervous system



- Damage to the immune system
- Psychological disorders
- Possibly DNA damage or cancer development.  
(<http://www.lenntech.com/Periodic-chart-elements/Cd-en.htm>)

### **1.2.3.3 Health effects of lead**

Lead is one out of four metals that have the most damaging effects on human health. It can enter the human body through uptake of food (65%), water (20%) and air (15%) (<http://www.lenntech.com/Periodic-chart-elements/Pb-en.htm>).

Foods such as fruit, vegetables, meats, grains, seafood, soft drinks and wine may contain significant amounts of lead. Cigarette smoke also contains small amounts of lead (<http://www.lenntech.com/Periodic-chart-elements/Pb-en.htm>).

Lead can enter (drinking) water through corrosion of pipes. This is more likely to happen when the water is slightly acidic. That is why public water treatment systems are now required to carry out pH-adjustments in water that will serve drinking purposes (<http://www.lenntech.com/Periodic-chart-elements/Pb-en.htm>).

For as far as we know, lead fulfils no essential function in the human body, it can merely do harm after uptake from food, air or water. Lead can cause several unwanted effects, such as:

- Disruption of the biosynthesis of hemoglobin and anemia
- A rise in blood pressure
- Kidney damage
- Miscarriage and subtle abortions
- Disruption of nervous systems
- Brain damage
- Declined fertility of men through sperm damage
- Diminished learning abilities of children

- Behavioral disruptions of children, such as aggression, impulsive behavior and hyperactivity (<http://www.lenntech.com/Periodic-chart-elements/Pb-en.htm>)

#### 1.2.4 Sources of heavy metals in atmosphere

Air pollution is generally related to gaseous emissions into the atmosphere (carbon monoxide, carbon dioxide, hydrocarbons, halocarbons, sulfur dioxide, hydrogen sulfide, nitrogen oxides, NO, NO<sub>2</sub>, N<sub>2</sub>O and ammonia). Heavy metals contamination can result primarily through atmosphere particles or particulates. The main sources of heavy metals in atmosphere (Table 1-5) are coal and fuel power generation plants, metal processing and smelting, transportational combustion, waste incineration, and aerosols spray (halocarbons). The major industrial emissions are non-ferrous metals-smelters, petroleum refining, cement production, chloro-alkali production, aluminum smelters and chemical production. The major examples of heavy metals can be released through industrial emissions are Cd, Pb, Fe, Ti, V, Mn, Fe, Cu, Cr, Ni and Zn (Ward, 1995).

Metal air pollution is of major concern in that it is global and contributes to contamination of all the components of the environment. In most cases the maximum pollution levels are within a few kilometers of the emission source but small particulate and aerosol pollutants can contaminate all areas of the earth (Ward, 1995). Heavy metals also contribute to the formation of photochemical smogs (Fe, V, Ca, Pb, Br, Cl). A mixture of metal particulates and acidic aerosols can directly affect human health through the increased incidence of eye and respiratory tract irritation, bronchitis and asthma (Ward, 1995).

A recent problem of metal particulate air pollution is their roles in the oxidation of sulfur dioxide and the formation of acidic aerosol involved in global acid rain. Many metals ions, such as Mn(II), Fe(III), Cu(II), Cr(III), Al(III) and Pb(II) act as catalysts in the reaction  $2\text{SO}_2 + 2\text{H}_2\text{O} + \text{O}_2 \longrightarrow 2\text{H}_2\text{SO}_4$ .

An ever increasing problem is the effect of atmospheric pollution and acid rain on the aquatic environment. Relatively pure rainwater has a pH of 5.5 but owing to SO<sub>2</sub> and NO<sub>2</sub> emissions, the pH of rain can drop as low as 2-3 (Ward, 1995).

**Table 1-5** Trace metals released into the atmosphere from human activities

Activity	F	Al	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Br	Mo	Ag	Cd	Sn	Sb	Hg	Ti	Pb
Coal and fuel power generation	√		√	√	√	√	√			√	√	√	√		√				√	√		
Metal processing and smelting	√	√		√	√	√	√	√	√	√	√	√	√		√	√	√	√	√	√	√	√
Transport				√	√	√		√	√	√	√			√			√		√	√		√
Waste incineration	√	√	√		√				√	√	√	√				√	√	√	√			√
Aerosol sprays		√									√						√					

Source: Adapted from Ward, 1995

### **1.2.5 Rainwater chemistry**

Most rainwater is not pure, although it is initially the product of natural distillation. Rainwater gathers impurities in several processes. It nucleates on aerosol particles many of which dissolve in the water thus altering the chemistry. As rain begins to form, rainwater interacts with various substances, dissolving some of substances. As the condensation and subsequent interaction processes are rainout. The rainout process produces a near constant chemistry in a given area at a given time. The other process that affects rainwater chemistry is washout. As the rain falls, it carries many particles to the ground with it. Most washouts occur early in the rainstorm (Warburton, 1991-2003).

#### **1.2.5.1 Formation of rain**

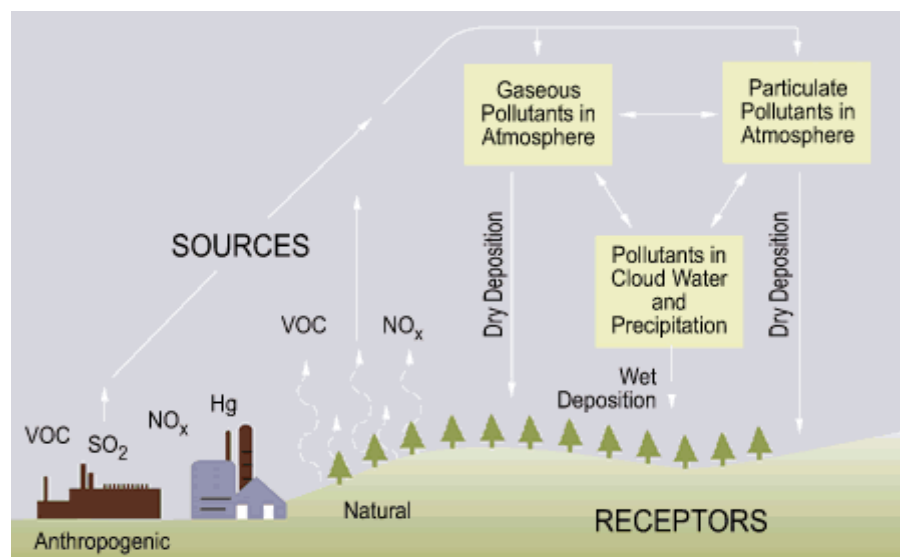
Most of the water in the atmosphere (more than 95%) is presented in the form of water vapor. The transformation of water vapor in the atmosphere into rain involves two processes. First, the water vapor gas must condense to form water droplets (or sublimate to form ice crystals). This is cloud or fog formation. In order for cloud droplets to fall to the ground as rain, they must become large and heavy enough to reach the ground without evaporation. The average lifetime of a cloud is around 1 hour; while on the average water spends 11 hours in the atmosphere in the form of droplets before being removed as rain. Thus, cloud water evaporates and condenses several times before actually forming rain. In order for condensation to occur, air must become supersaturated with water vapor, but this is not enough. Nuclei are needed to begin the condensation process and second, instead of forming water droplets, water vapor is transformed to ice crystals via the process of sublimation whenever the temperature is sufficiently cold, as often occurs at the tops of clouds. However, because ice crystals nucleate with much greater difficulty than water droplets, temperatures considerably lower than 0°C are necessary for sublimation to occur (Berner, 1996).

The water droplets in most clouds average about 5-10  $\mu\text{m}$  in diameter, with the largest being about 20  $\mu\text{m}$  in diameter. Because of constant updrafts, these

sizes are too small for the droplets to fall to the ground. In order to have rain, there must be a process whereby the droplets can become big enough, on the average about 1000  $\mu\text{m}$  in diameter, to fall as rain drops (Berner, 1996).

Atmospheric deposition refers to the removal of pollutants from the air to soil, water and other surfaces. Deposition to water bodies can occur directly to the surface or indirectly, when material deposited to the land surface enters a water body through runoff. The major processes in atmospheric deposition are wet deposition and dry deposition is show in Figure 1-2

(<http://www.delta-institute.org/publications/airtoxics.pdf>).



**Figure 1-2** Adapted from illustrations of atmospheric depositional processes (<http://www.epa.gov/airmarkets/acidrain/>)

### 1.2.5.2 Wet deposition

Wet deposition refers to the incorporation of both gases and particles into all types of precipitation: rain, fog or snow. Pollutants may be removed from air by wet deposition through three main mechanisms:

1. Small particles can serve as cloud condensation nuclei and become entrapped in raindrops.
2. Particles can be incorporated into falling raindrops by a variety of mechanisms depending on their size, referred to as particle scavenging.

3. Gaseous pollutants can be dissolved into cloud droplets and falling rain or snow.

Trace metals and semi-volatile organic chemicals (chemicals that can exist either as a gas or associated with particles) can become associated with rain either by being dissolved in the raindrop or by being incorporated as particles (<http://www.delta-institute.org/publications/airtoxics.pdf>).

### **1.2.5.3 Dry particle deposition**

Dry particle deposition is broadly defined as the transport of particles and the contaminants associated with them onto surfaces. In general, the amount of contaminants deposited depends on concentrations in the air mass. The relation is complex, however, depending on such physical factors as wind speed, the area of the receiving surface and whether that surface is water or land, and the properties of the contaminant, such as reactivity and the size of the particle with which it is associated (<http://www.delta-institute.org/publications/airtoxics.pdf>).

### **1.2.5.4 Chemical composition of rainwater: General characteristics**

The major dissolved element composition of a large number of rainfalls is presented in Table 1-6.

The dissolved chemical components of rainwater can be divided into two groups: (1) those derived primarily from particles in the air ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Cl}^-$ ) and (2) those derived mainly from atmospheric gases ( $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$  and  $\text{NO}_3^-$ ) (Berner, 1996).

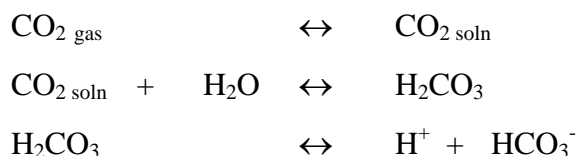
**Table 1- 6** Primary Associations in Rain

Origin	Associations
Marine inputs	Cl -Na - Mg -SO <sub>4</sub>
Soil inputs	Al -Fe-Si-Ca- (K, Mg, Na)
Biological inputs	NO <sub>3</sub> -NH <sub>4</sub> - SO <sub>4</sub> -K
Biomass burning	NO <sub>3</sub> -NH <sub>4</sub> - P - K - SO <sub>4</sub> - (Ca, Na, Mg)
Industrial pollution	SO <sub>4</sub> - NO <sub>3</sub> - Cl
Fertilizers	K -PO <sub>4</sub> -NH <sub>4</sub> -NO <sub>3</sub>

Source: Berner (1996)

### 1.2.5.5 The pH of natural rainwater

Pure water containing no dissolved substances should have a pH of 7, in which case it is referred to as being neutral (neither acidic nor basic). Natural rainwater, however, is not pure water. First of all, as a result of the solution of atmosphere carbon dioxide (to equilibrium), rainwater becomes moderately acidic, with a pH of 5.7. This comes about from the reaction of CO<sub>2</sub> with H<sub>2</sub>O, which results in the formation of carbonic acid, H<sub>2</sub>CO<sub>3</sub>, which in turn partly dissociates to produce hydrogen and bicarbonate ions (further dissociation of HCO<sub>3</sub><sup>-</sup> to CO<sub>3</sub><sup>2-</sup> and H<sup>+</sup> is negligible at the pH of rain)(Berner, 1996):



### 1.2.6 Limits and analysis of metals

Several techniques were used to analyze heavy metals in rainwater samples, Atomic absorption spectrometry (flame or electrothermal) is a widely used and accepted technique capable of determining trace ( $\mu\text{g mL}^{-1}$ ) and ultra trace (sub- $\mu\text{g mL}^{-1}$ ) levels of elements or metals in a variety of samples including biological, clinical, environmental, food and geological samples, with good accuracy and acceptable precision (Sneddon, 1997). Graphite furnace atomic absorption spectrometry is technique was used to determine metals in solution. This method is simple, quick and applicable to a large number of metals in environmental samples including, but not limited to, ground water, domestic and industrial wastes,

extracts, soils and sediments. With the exception of the analyses for dissolved constituents, all samples require digestion before analysis. Analysis for dissolved elements does not require digestion if the sample has been filtered and then acidified (EPA method 7010).

Several techniques for determination of heavy metals in rainwater samples are shown in Table 1-7.

**Table 1-7** Techniques for determination of heavy metals in rainwater samples

Metals	Technique	References
Pb, Cd and Zn	DPASV*	Kanatharana and Chareonchatchai, 1985
Cu, Pb and Zn	FAAS	Nyika <i>et al.</i> , 1996
Cu and Pb	ASV	Struck <i>et al.</i> , 1996
Al, Ba, Cd, Cu, Mn, Pb, Sr, V and Zn	ICP-MS	Takeda <i>et al.</i> , 2000
Zn, Pb, Cu, Ni, Sb, Cd and Rb	ICP-MS	Roy and Negrel, 2001
Cd, Cr, Cu, Ni, Pb, V and Zn	GFAAS	Morselli <i>et al.</i> , 2003

\* DPASV = Differential pulse anodic stripping voltammetry

In this work, GFAAS is used to determine of Cu, Cd and Pb in rainwater samples.

## 1.2.7 Graphite furnace atomic absorption spectrometry

The sensitivity of graphite furnace atomic absorption makes it the obvious choice for trace metal analysis applications. Routine determinations at the  $\mu\text{g L}^{-1}$  level for most metals make it ideal for environmental applications (Beaty and Kerber, 1993).

### 1.2.7.1 Components of the graphite furnace system

The graphite furnace is made up of the three major components, the atomizer, the power supply and the programmer. The atomizer is located in the



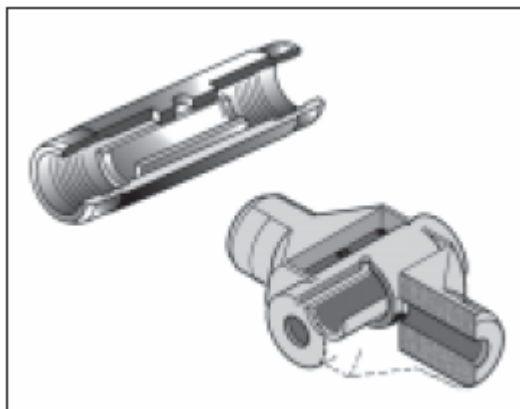
sampling compartment of the atomic absorption spectrometer, where sample atomization and light absorption occur. The power supply controls power and gas flows to the atomizer under the direction of the programmer, which is usually built into the power supply or spectrometer (Beaty and Kerber, 1993).

#### **1.2.7.1.1 The graphite furnace atomizer**

A basic graphite furnace atomizer is comprised of the following components:

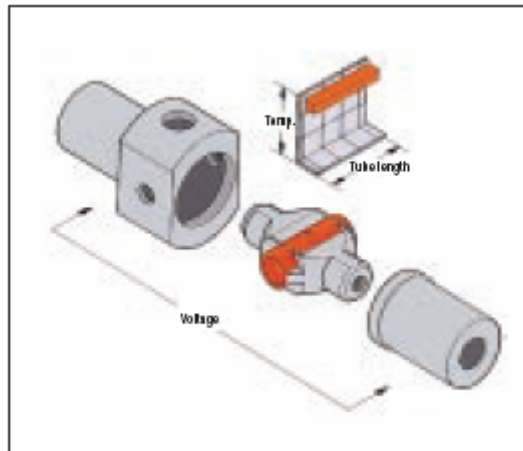
- Graphite tube
- Electrical controls
- Enclosed water cooled housing
- Inert purge gas controls

A graphite tube is normally the heating metal of the graphite furnace. The cylindrical tube is aligned horizontally in the optical path of the spectrometer and serves as the spectrometer sampling cell. A few micro liters (usually 5-50) of sample are measured and dispensed through a hole in the center of the tube wall onto the inner tube wall or graphite platform. The tube is held in place between two graphite contact cylinders, which provide electrical connection. An electrical potential applied to the contacts cause current to flow through the tube, the effect of which is heating of the tube and the sample (Beaty and Kerber, 1993). The HGA and THGA graphite tubes with integrated L'vov platform for larger sample volumes are shown in Figure 1-3.



**Figure 1-3** HGA and THGA graphite tubes with integrated L'vov platform for larger sample volumes (Source: The Perkin-Elmer AAnalyst 700 and 800 Atomic Absorption Spectrometer, 1997)

The entire assembly is mounted within an enclosed, water-cooled housing. Quartz windows at each end of the housing allow light to pass through the tube. The heated graphite is protected from air oxidation by the end windows and two streams of argon. An external gas flow surrounds the outside of the tube, and a separately controllable internal gas flow purges the inside of the tube. The system should regulate the internal gas flow so that the internal flow is reduced or preferably, completely interrupted during atomization. This helps to maximize sample residence time in the tube and increase the measurement signal. The transversely-heated graphite furnace (Figure 1-4) eliminates many of the problems associated with the longitudinally-heated furnace. The graphite tube of the transversely-heated graphite includes integral tabs which protrude from each side. These tabs are inserted into the electrical contacts. When power is applied, the tube is heated across its circumference (transversely). By applying power in this manner, the tube is heated evenly over its entire length, eliminating or significantly reducing the sample condensation problems seen with longitudinally- heated furnace systems.



**Figure 1-4** The transversely heated graphite tube provides a uniform temperature profile  
(Source: The Perkin-Elmer AAnalyst 700 and 800 Atomic Absorption Spectrometer, 1997)

An additional advantage of the transversely-heated furnace is that it allows the use of longitudinal Zeeman-effect background correction. Longitudinal Zeeman offers all of the advantages of transverse Zeeman correction with put the need to include a polarizer in the optical system. This provides a significant improvement in light throughput (Beaty and Kerber, 1993).

#### 1.2.7.1.2 The graphite furnace power supply and programmer

The power supply and programmer perform the following functions:

- electrical power control
- temperature program control
- gas flow control
- spectrometer function control

The power supply controls the electrical current supplied to the graphite tube, which causes heating. The temperature of the tube is controlled by a user-specified temperature program. Through the programmer the operator will enter a sequence of selected temperatures vs. time to carefully dry, pyrolyze, and finally atomize the sample. The program may also include settings for the internal gas flow

rate and, in some cases, the selection of an alternate gas. Certain spectrometer functions, such as triggering of the spectrometer read function, also may be programmed and synchronized with the atomization of the sample in the furnace (Beaty and Kerber, 1993).

### **1.2.8 Solid phase extraction**

Despite the high sensitivity of GFAAS, there is crucial need for the preconcentration of trace metals before analysis due to frequent low concentrations in rainwater samples. Various methods used for preconcentration are liquid-liquid extraction, precipitation technique, freezing-based concentration methods, carbon adsorption, distillation, sublimation, evaporation and the use of ion exchange resins (Cheng *et al.*, 1994).

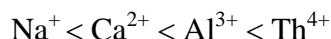
Liquid-liquid extraction (LLE) is a classical method for preconcentrating metal ions and/or matrix removal. Liquid-liquid extraction is a method of separation based on the transfer of a solute from one solvent into another, essentially immiscible solvent when the two solvents are brought into contact. The reason for the large popularity of liquid-liquid extraction lies in the speed, ease and convenience of the technique (Freiser, 1973).

Solid phase extraction (SPE) is another approach that offers a number of important benefits. It reduces solvent usage and exposure, disposal costs and extraction time for sample preparation. The principle of SPE is similar to that of liquid-liquid extraction, 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 (Camel, 2003).

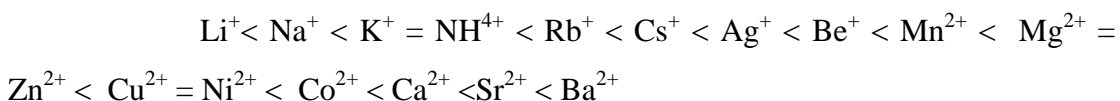
Ion-exchange resins are the most suited for trace elements analysis. They are of several types, such as cation exchangers, anion exchangers and chelating resins. Ion exchange is a process in which one type of ion in a compound is exchanged for a different type: cation for cation and anion for anion (Ohzeki, 1995).

### General rules for ion exchange affinity

1. At low concentrations and ordinary temperatures, the extent of exchange increases with increasing valency of the exchanging ion.



2. At low concentrations, ordinary temperatures, and constant valence, the extent of exchange increases with increasing atomic number of the exchanging ion.



3. At high concentrations, the differences in the exchange potential of ions of different valences ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ) diminishes, and in some cases reverses. This is how resins can be regenerated.

4. At high temperature, in non aqueous media, or at high concentration, the exchange potentials of ions of similar charge become quite similar and even reverse.

5. The relative exchange potentials of various ions can be approximated from their activity coefficients; the higher the activity coefficients, the greater the exchange is.

6. The exchange potentials of the  $\text{H}^+$  and  $\text{OH}^-$  ions varies considerably with the nature of the functional group and depend upon the strength of the acid or base formed between the functional group and either the hydrogen or hydroxyl ion. The stronger the acid or base, the lower the exchange potential.

In recent years, the use of chelating resins has extensively. In general, chelating resins are a group of materials having complexing or chelating groups on their surface, e.g., Chelex-100 (Garg *et al.*, 1999).

Chelating resins are distinguished from the ordinary type of ion exchange resins by their high selectivity and the firmness with which they bind elements. The selective properties of chelating ion exchangers to particular metal ions are mainly based on the nature of the chelating groups, and depend to a minor extent on the size, charge, and other physical properties of the ions (Ohzeki, 1995).

Sorption selectivity is also affected by the properties of the resin matrices and the mutual disposition of the functional groups and in some cases also the remoteness from the matrix. The exchange process in a chelating resin is often

slower than in ordinary ion exchanger, e.g. strongly acidic or basic resins. The rate at which element ions are absorbed is determined both by diffusion and by complex formation reactions and depends on the properties of matrix, the nature of the ion being adsorbed, and that of chelate group (Ohzeki, 1995).

Several functional group atoms are capable of chelating trace metals. The atoms most frequently used are nitrogen (e.g. N present in amines, azo groups, amides, nitriles), oxygen (e.g. O present in carboxylic, hydroxyl, phenolic, ether, carbonyl, phosphoryl groups) and sulfur (e.g. S present in thiols, thiocarbamates, thioethers). The nature of the functional group will give an idea of the selectivity of the ligand towards trace metals. In practice, inorganic cations may be divided into 3 groups:

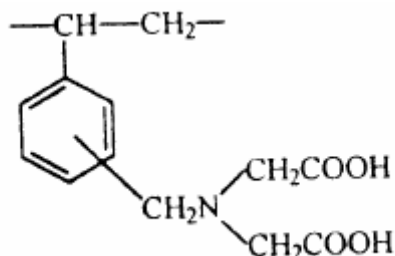
- group I- “hard” cations: these preferentially react via electrostatic interactions (due to a gain in entropy caused by changes in orientation of hydration water molecules); this group includes alkaline and alkaline earth metals ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ) that form rather weak outer-sphere complexes with only hard oxygen ligands.
- group II-“borderline” cations: these have an intermediate character; this group contains  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Mn}^{2+}$ . They possess affinity for both hard and soft ligands.
- group III-“soft” cations: these tend to form covalent bonds. Hence,  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$  possess strong affinity for intermediate (N) and soft (S) ligands (Camel, 2003).

Binding of metal ions to the chelate functionality is dependent on several factors:

- (1) nature, charge and size of the metal ion
- (2) nature of the donor atoms present in the ligand
- (3) buffering conditions which favor certain metal extraction and binding to active donor or groups
- (4) nature of the solid support (e.g. degree of cross-linkage for a polymer) (Camel, 2003)

The resins containing iminodiacetic acid (Figure 1-5) as a functional group are most widely used to separate transition metals from alkali and alkaline earth elements and to separate pairs and groups of heavy metals. They are commercially

available under different trade names, namely Dowex A-1, Chelex- 100, IRC-718 etc. (Ohzeki, 1995).



**Figure 1-5** Iminodiacetic acid immobilised on styrene matrix (Garg *et al.*, 1999)

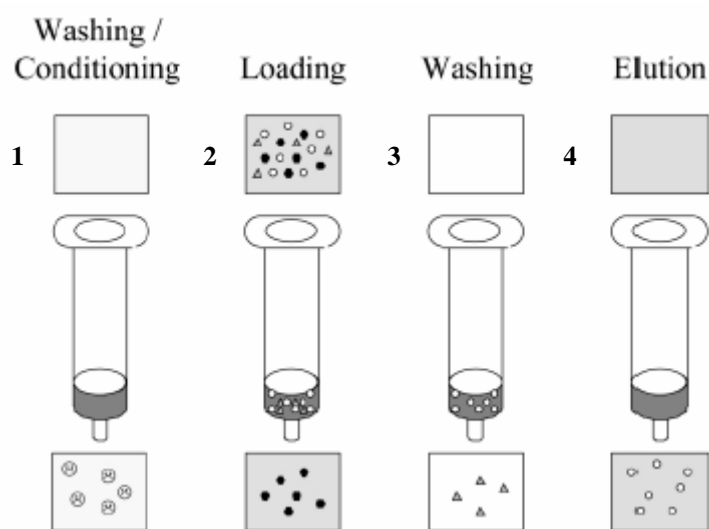
The iminodiacetic acid group could provide electron pairs so that the binding forces for alkali earth metals is 5000 times than those for alkali metals like  $\text{Na}^{2+}$ , which can react with divalent metals to form a stable coordination covalent bond (Lin and Juang, 2005).

Amberlite IRC-748 (formerly, IRC-718) is another chelating resin which have been extensively reported to be bonded to the iminodiacetate acid functional groups. Amberlite IRC-748 has a high affinity for heavy metal ions (Malla *et al.*, 2002).

In this work, Amberlite IRC-748 was chosen as chelating resin for the preconcentration of Cu, Cd and Pb in rainwater samples and analyzed by graphite furnace atomic absorption spectrometer (GFAAS).

An SPE method always consists of three or four successive steps as illustrated in Figure 1-6; First, the solid sorbent should be conditioned using an appropriate solvent, followed by the same solvent as the sample solvent. This step is crucial, as it enables the wetting of the packing material and the solvation of the functional groups. The second step is the percolation of the sample through the solid sorbent. Depending on the system used, volumes can range from 1 mL to 1 L. The sample may be applied to the column by gravity, pumping, aspirated by vacuum or by an automated system. The sample flow rate through the sorbent should be low enough to enable efficient retention of the analytes, and high enough to avoid excessive duration. The third step may be the washing of the solid sorbent to

eliminate matrix components that have been retained by the solid sorbents, without displacing the analytes. The final step consists in the elution of the analytes of interest by an appropriate solvent, without removing retained matrix components. The solvent volume should be adjusted so that quantitative recovery of the analytes is achieved with subsequent low dilution (Camel, 2003).



**Figure 1-6** Solid phase extraction operation steps (Camel, 2003)

### 1.2.9 General information of Hat Yai City municipality, Songkhla Province

Hat Yai is a city in Songkhla Province southern Thailand near the border to Malaysia. Geographical location  $7^{\circ}1'$  and  $100^{\circ}28'$  with a population of 157,678 (2005 census). Location of big emission sources in Songkhla Province is show in Table1-8.



**Table 1-8** Location of big emission sources in Songkhla Province

Industry factory	Use energy (hp)	Latitude	Longitude
Safe Skin Medical and Scientific Ltd.	140,748	6° 39'	100° 25'
Safe Skin Corporation Ltd.	83,957	6° 50'	100° 27'
Siam Sampermed Ltd. (factory 2)	46,204	6° 39'	100° 26'
Tropical Canning (Thailand) Public Company Ltd.	26,483	7° 07'	100° 34'
Siam Sampermed Corp. Ltd.	18,892	6° 39'	100° 26'
Chareon Pokphand Ltd.	17,821	6° 58'	100° 29'
Chotiwat Manufacturing Co., Ltd.	17,077	7° 04'	100° 32'
Omnigrace (Thailand) Ltd.	16,613	6° 58'	100° 29'
Songkhla Canning Public Co., Ltd.	15,557	7° 07'	100° 34'

Source: Songkhla Provincial Industry Office, 2003

### 1.2.9.1 Topography of Songkhla Province

The north of Songkhla Province is a narrow peninsula and long to south to call Sathingpra peninsula with a rectagle area in south. Two areas are joined by Tinnasulanon Bridge. Most north area of Songkhla Province is a plain. The east area of Songkhla Province is a seaside plan. The south and west of Songkhla Province is a mountain highland the source of major streams. The map of Songkhla Province is shown in Figure 1-7.

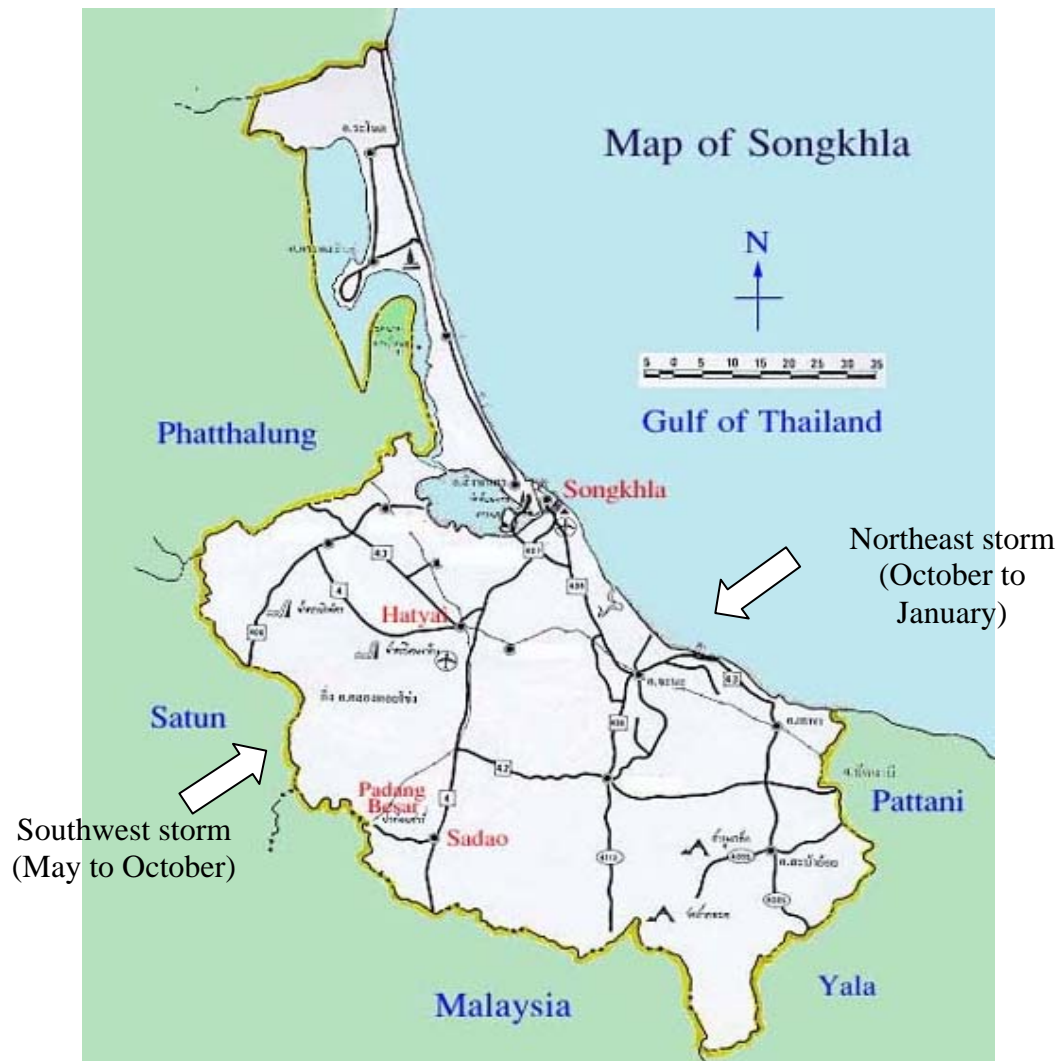
### 1.2.9.2 Climate of Songkhla Province

Songkhla Province received rainstorm every year such as northeast storm begin in October to January and a southwest storm begin in middle of May to in middle of October.

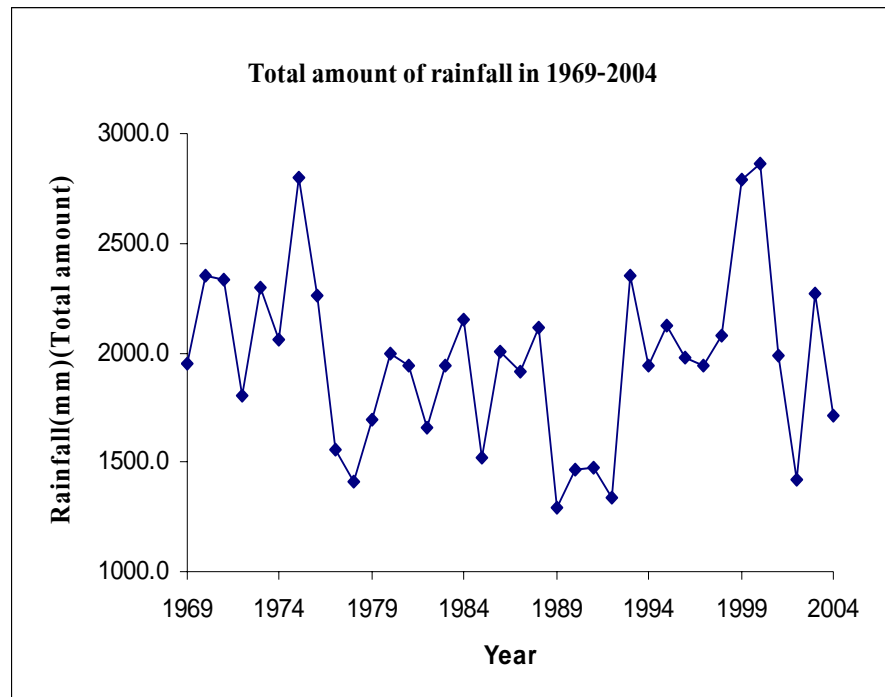
Songkhla Province has two seasons; dry season from February to July and rainy season from August to January.

In 2002, Songkhla Province have total amount of rainfall was 1,399.1 mL, amount of days with rainfall was 142 days, in November the highest rainfall was 503.4 mL and in February have a few rainfall was 1.5 mL.

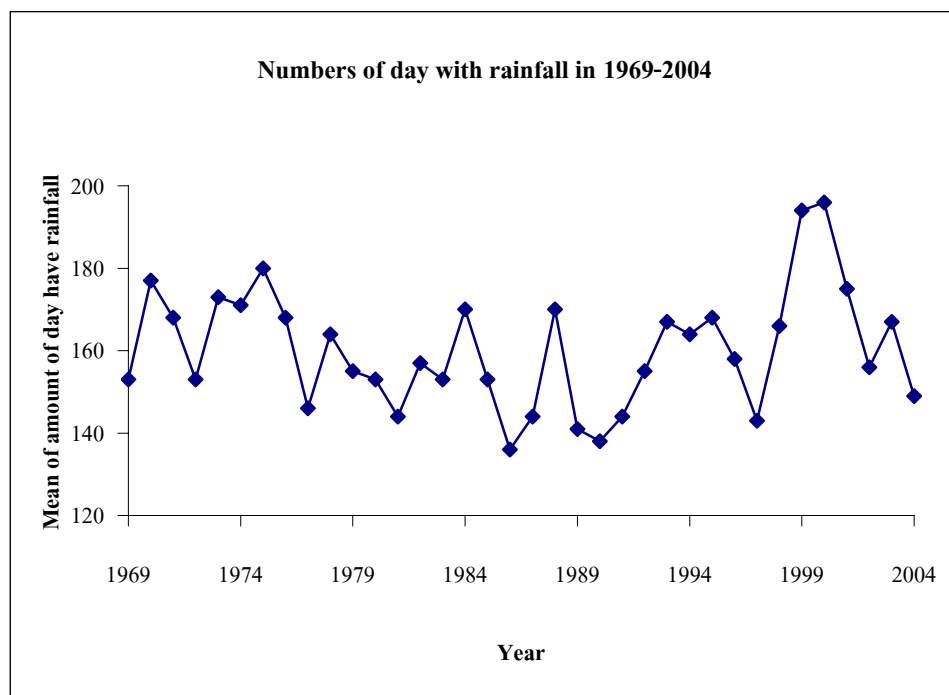
The average temperature was 28 °C, the maximum temperature on the average was 36 °C on July 14th and minimum temperature on the average was 23 °C on March 16th (<http://www.rubber.co.th/songkhla/service/skarea.htm>). Total amount of rainfall in 1969-2004 is show in Figure 1-8 and amount of day with rainfall in 1969-2004 is show in Figure1-9.



**Figure 1-7** Map of Songkhla Province (<http://www.bangkoksite.com/Songkhla/>)



**Figure 1-8** Total amount of rainfall in 1969-2004  
 (<http://www.rubber.co.th/songkhla/service/skarea.htm>)



**Figure 1-9** Numbers of day with rainfall in 1969-2004  
 (<http://www.rubber.co.th/songkhla/service/skarea.htm>)

### 1.3 Literature reviews

In recent years, many researchers concentration of heavy metals in rainwater in order to evaluated levels of heavy metals deposition from the main sources of contamination.

Kanatharana and Chareonchatchai, 1985 reported the concentrations of Pb, Cd and Zn in rainwater samples collected from five stations around Hat Yai and ten samples for each station. The samples were analyzed by technique of differential pulse anodic stripping voltammetry (DPASV). The concentration of Pb, Cd and Zn found are 0.010-0.045 mg L<sup>-1</sup>,  $1.63 \times 10^{-4}$ - $2.23 \times 10^{-3}$  mg L<sup>-1</sup> and 0.008-0.022 mg L<sup>-1</sup>, respectively. Those with the highest values were samples collected near industrial area.

Struck *et al.*, 1996 reported the atmospheric dispersion and physicochemical behaviour of Cd and Pb after emission from the lead works at Stolberg - Binsfeldhammer, Germany. Measurements of wet deposition were made with rainwater samples between Stolberg and the town of Julich to the northeast during the period August 1991- May 1992. Analysis of rainwater after filtration in the rain sampler comprised heavy metal concentrations in the residue as well as heavy metal in the filtrate. Cadmium and Pb compounds analyzed have total concentrations in the rainwater with are smaller than their respective solubilities. In the case of Cd, dissolved Cd was found large amount in rainwater dominates and Pb could also be responsible for the relatively large amount of Pb adsorbed on solid particles.

Nyika *et al.*, 1996 reported the status of the atmospheric environment was assessed by characterization of composite precipitation samples collected during 1991-1992 and single event samples in 1992-1993 rainy seasons in Bulawayo, Zimbabwe. A typical single event precipitation sample from 10th January 1993 had pH 6.87 and conductance 4.6  $\mu\text{scm}^{-1}$ . The concentrations of anions and cations ( $\mu\text{g L}^{-1}$ ) were sulfate (271.68), chloride (134.55), nitrate (71.92), bicarbonate (801.54), ammonium (10.26), potassium (35.49), sodium (86.94), calcium (346.8),

magnesium (30.24),  $H^+$  (0.38), copper (1.143) and zinc (3.66).

Ezat *et al.*, 1997 reported assess the wet deposition of aerosols of different origins in the eastern Mediterranean. The most of Al wet deposition is associated with a few African dust transport events during springtime. Such events are associated with high rainwater pH values, up to more than 8. Lead concentrations could only be determined in samples collected near Heraklion with ranging from 2 to  $32 \mu\text{g L}^{-1}$  and large values were found whatever the pH of rain, suggesting important influence from the local urban pollution.

Garnaud *et al.*, 1999 reported the metal concentrations of atmospheric deposits collected at four sites inside the Paris conurbation, either in the suburb or the center of the city. Dry and wet deposits have been measured. The dissolved metal distribution in rainwater: lower-upper decile range of dissolved total metal ratio (%) for Cd, Cu, Pb and Zn was 75-100, 57-100, 63-90 and 84-100, respectively. Comparison of metal contamination of wet fallout samples simultaneously at the Paris centre and at 48 nkm apart that their levels were only significantly lower for copper and lead. This demonstrates the importance of urban plumes of atmospheric pollution. Although these bulk metal levels were not higher than in other urban sites, they present a major concern for the environment: metals are almost entirely dissolved and consequently, under bioavailable and toxic forms.

Takada *et al.*, 2000 reported the concentrations of 14 elements (Al, Ba, Ca, Cd, Cu, Mg, Mn, Na, Ni, Pb, Sr, V and Zn) and 5 ions ( $Cl^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$ ,  $NH_4^+$  and  $H^+$ ) in wet depositions were collected in Higashi-Hiroshima in western Japan for 3 years (1995-1997). Concentrations of heavy metals were measured by inductively coupled plasma mass spectrometry (ICP-MS). The concentration of Al, Cd, Cu, Pb, Mn, Ni, V and Zn was 0.06, 0.063, 0.62, 1.24, 1.64, 0.29, 0.23 and  $4.77 \mu\text{g L}^{-1}$ . The characteristic variations of these species were investigated in terms of the source of atmospheric heavy metals. The elements were classified into three categories by principal component analysis, constituents from an anthropogenic source (Cd, Cu, Pb, V, Zn,  $NO_3^-$ ,  $SO_4^{2-}$ ,  $NH_4^+$  and  $H^+$ ), elements associated with crustal source (Al, Ba, Cd

and Mn) and elements from sea salts (Na, Mg and Cl<sup>-</sup>). The depositions and concentrations of the elements associated with soil dust were peculiarly enhanced in the spring.

Roy and Negrel, 2001 reported the lead isotope ratios and Zn, Pb, Cu, Cd, Sb and Rb contents were measured in rainwater samples collected over a period of 15 months from the Massif Central (France). Each sample, collected automatically at monthly intervals, represents a series of rainfall events. Rainwater chemistry was interpreted in terms of the chemical contributions from wet deposition and from different source regions for dust in the centre of France. The samples were analyzed by technique of ICP-MS. Trace element concentrations in rainwater samples was a wide range, particularly for Pb (1.30-465  $\mu\text{g L}^{-1}$ ), with variations decreasing for Cd (0.07-1.70  $\mu\text{g L}^{-1}$ ), Zn (1.00-54.00  $\mu\text{g L}^{-1}$ ), Cu (0.20-25.00  $\mu\text{g L}^{-1}$ ), Sb ( $\sim$  -0.33  $\mu\text{g L}^{-1}$ ) and Ni ( $\sim$ 0-15.00  $\mu\text{g L}^{-1}$ ). Trace element contents do not correlate with rainfall amount and no inter-element correlations are evident in the data.

Kanellopoulou, 2001 reported the concentrations of 10 metals are determined (Pb, Cd, Ni, Cr, Al, Cu, Zn, Mn, Fe, As) in October 1997 to March 1998 at Ilissia station of Athens University Campus (AUC) in Greece, were relatively low with the exception of the Zn. Using Spearman correlation method and the technique of Principal Component Analysis, it was found that the metals Cd, Ni, Cr, Cu, Zn, Mn and Fe have common sources (the industrial area of Thriasio basin at the west of Athens or the National Highway and the factories at the north and northeast of Athens). The source of Pb must be near the station (the traffic circulation around the University campus), while Al and as seem to have their own common source. The possible origin of Al is the soil erosion and the mines of Lavrio, at the greater vicinity of Athens, are the possible source of As.

Liu *et al.*, 2003 reported 120 rainwater samples were collected from Qianliyan island (Yellow Sea) and Shengsi island (East China Sea) from May 2000 to May 2002. The samples were analyzed for pH values and determined the concentrations of heavy metals (Cu, Pb, Zn and Cd) by Flame/Graphite absorption

spectrometry. The results indicate that the concentrations of most heavy metals in rainwater show a clear seasonal variation with higher levels in winter and lower level in summer. Generally, the heavy metal concentrations in rainwater are higher at Qianliyan than at Shengsi island and the yearly atmospheric wet depositions fluxes of heavy metals are larger than those at Shengsi island, in spite of the annual rainfall is smaller at Qianliyan island relative to the Shengsi. At Qianliyan, Pb is inputed into the sea mainly by dry deposition whereas for Cu, Zn and Cd, wet deposition plays an important role for heavy metals transported to the ocean at the Yellow Sea regions.

Agraz *et al.*, 1993 reported a carbon paste electrode modified with Amberlite IRC-718 resin, containing the chelating agent iminodiacetic acid, was used for speciation analysis. Copper was accumulated on the electrode surface when the electrode was immersed in the sample and then the amount of copper preconcentrated was evaluated by cyclic voltammetry. The chemical reaction studied is based on exchange of the iminodiacetate group attached to the electrode surface with the competing ligand in solution. A kinetic study allowed the determination of the influence of the nature of the interfering ligand on the reaction rate. A comparison of the results obtained by this method with theoretical predictions based on thermodynamic equilibrium constants and nature ligand classification as a function of their effects was reported.

Malla *et al.*, 2002 reported the Amberlite IRC-718 containing iminodiacetate groups as active sites, has been characterized regarding the sorption and subsequent elution of Cd, Pb and Zn, aiming to metal concentration from solution samples of different origins. The methodology developed is based on off-line operation employing minicolumns made of the sorbent. The eluted metals were determined by flame atomic absorption spectrometry.

Lin and Juang, 2005 reported the two chelating ion exchange resins Chelex-100 and Amberlite IRC-748 (formerly, IRC-718) which have iminodiacetate acid (IDA) functional groups were used to exchange Cu (II) and Zn (II) from aqueous



solutions. Batch experiments were using the Na-form resins by varying the initial concentration of metals ( $0.8-10.5 \text{ mol m}^{-3}$ ), initial aqueous pH (1.0-5.0) and temperature (15-45 °C).

## **1.4 Objectives**

The aims of this research are:

- 1.4.1 To optimize conditions of graphite furnace atomic absorption spectrometer (GFAAS) for determination of Cu, Cd and Pb.
- 1.4.2 To optimize conditions for preconcentration of Cu, Cd and Pb by using Amberlite IRC-748 chelating resin.
- 1.4.3 To use conditions for preconcentration and optimum conditions of GFAAS for the determination of Cu, Cd and Pb in rainwater samples in Hat Yai City Municipality.