CHAPTER 1

INTRODUCTIONS

1.1 Introduction

Acid deposition or well known in the term of Acid rain is a global environmental issue, which has serious discussion by many scientists to find out its solution. The acidic pollutants can travels over long distance in clouds. Therefore, acid rain does not just affect the area where it originates. Every area with a power station or significant number of road vehicles can generates air pollutions, which cause an acid rain phenomenon. The acid particles can be transfer further by wind blows and monsoon. Therefore countries that are not produced the acid gases can get the effect from acid deposition by moving of monsoon that carry the pollutant gases to spread over on their route.

In the 1850's, researchers in England described the presence of both nitric and sulfuric acid in air. The term of "Acid Rain" was use as early as 1872 in a book titled "Air and Rain: The beginnings of chemical climatology" publish by R.A. Smith in England (Bubenick, 1984). These pollutants are emitted from natural and anthropogenic sources. However, anthropogenic source are take place as the major of them in atmosphere as 90% for sulfur dioxide and 95% for nitrogen dioxide (Sher, 1998).

In Europe and North America, acid deposition has seriously affected water and forests in some areas and also occurred in East Asia. Hirochi (1998) studied acid deposition chemistry in these areas. His work showed the trend of acid deposition in terms of concentration and deposition of nitrate (NO_3^-), sulfate (SO_4^{2-}) and pH in many part of the world. Even if the European and other develop countries have reduced the level of acidic emission but their trends in Asia are still increasing. A study of Hiroaki (2001) on a trend of acid rain in East Asia found the drastic increase of acidity of precipitation due to the rapid increase of the pollutants emission in China from 1985 to 1995. Most industrialized countries have effectively cut SO_2 emissions to help mitigate the damage of acid rain on ecosystems. But the acid rain problem is not yet solved because emissions of nitrogen oxides have remained constant or are rising in North America and Europe. At the same time, acid rain is emerging as a major problem in the developing world, especially in parts of the Asia and the Pacific region where energy use has surged. (http://earthtrends.wri.org)

Acid rain has a variety of effects such as damage of the terrestrial ecosystem (as soils, flora and fauna), aquatic ecosystem (as reservoir, fish), materials, and human health. Significantly effect of acid deposition in Thailand was experienced since year 1992, due to SO_2 emitted from the Mae Moh lignite-fired power plant in Lampang province in the northern part. The raw material of this power plant is lignite, which contains high-sulfur average as 3% by weight (http://www.pcd.go.th). The power plant burned lignite to generate electricity without any SO_2 emission control system. An accumulated of SO_2 in atmosphere damaged a hundred of rai of village's rice field and effect to human health. There were 400 villagers near the power plant reported, respiratory symtom believed that caused by air pollution. According to these serious problems, the solutions were established. Establish of monitoring station is one of the solutions of Thai government. The monitoring network has been set up with other countries in East Asia call as Acid Deposition Monitoring Network in East Asia (EANET) in order to monitor and perform database of acid deposition in this region.

1.2 Rain component

Pure water has a pH around 7.0 but most rainfall is slightly weak acidic at pH 5.6 due to carbonic acid from carbon dioxide (CO_2) content of the atmosphere dissolves in rain water.

$$CO_2(g) + H_2O \quad \rule{2cm}{0.4pt} \quad H_2CO_3(l)$$

$$H_2CO_3(l) \quad \rule{2cm}{0.4pt} \quad H^+ + HCO_3^-$$

Normally, the component of rainwater consists of gases, aerosol and particles containing in ambient air. The source of ions containing in rain water are shown in Table 1.1.

Table 1.1 Source of ions containing in rainwater (Canter, 1986)

Ion	**Origin**		
	Marine input	**Terrestrial input**	**Pollutive input**
Na^+	Sea salt	Soil dust	Bio-mass burning
Mg^{2+}	Sea salt	Soil dust	Bio-mass burning
K^+	Sea salt	Biogenic aerosols Soil dust	Bio-mass burning Fertilizer
Ca^{2+}	Sea salt	Soil dust	Cement manufacture Fuel burning Bio-mass burning

Table 1.1 Source of ions containing in rainwater (Continued)

Ion	**Origin**		
	Marine input	**Terrestrial input**	**Pollutant input**
H^+	Gas reaction	Gas reaction	Fuel burning
Cl^-	Sea salt	-	Industrial HCl
SO_4^{2-}	Sea salt DMS from biological decay	DMS, H_2S etc., from biological decay Volcanoes	Fossil fuel burning Bio-mass burning
NO_3^-	N_2 Plus lightning	Soil dust NO_2 from biological decay	Auto emissions Fossil fuels Bio-mass burning Fertilizer
NH_4^+	NH_3 from biological activity	N_2 Plus lightning NH_3 from bacterial decay	NH_3 fertilizer Human, animal waste decomposition (Combustion)
PO_4^{3-}	Biogenic aerosols	Soil dust	Bio-mass burning
HCO_3^-	Adsorbed on sea salt CO_2 in air	CO_2 in air Soil dust	Bio-mass burning
SiO_2, Al, Fe	-	Soil dust	Fertilizer Land clearing

1.3 Acidity

The simply way to measure acidity of solution can be done by pH (potential hydrogen) measurement. The definition of pH is the negative logarithm of the hydrogen ion concentration.

$$pH = -\log\left[H^{+}\right]$$

The pH value of a substance is directly related to the ratio of the hydrogen ion [H^+] and the hydroxyl ion [OH^-] concentrations.

If the H^+ concentration is greater than OH^-, the material is acidic; i.e., the pH value is less than 7. If the OH^- concentration is greater than H^+, the material is basic or alkaline, with a pH value greater than 7. If equal amounts of H^+ and OH^- ions are present, the material is neutral, with a pH of 7. Thus, pH is a measurement of both acidity and alkalinity, even though by definition it is a selective measurement of hydrogen/hydroxyl ion activity. Figure 1.1 shows the pH scale, a change of one unit indicates a ten-time increase or decrease in the pH of a solution. Therefore, a solution with a pH of 3.0 is ten times more acidic than one of pH 4.0, while a solution with a pH of 3.0 is one hundred times more acidic than one of pH 5.0. (http://oldweb.northampton.ac.uk).

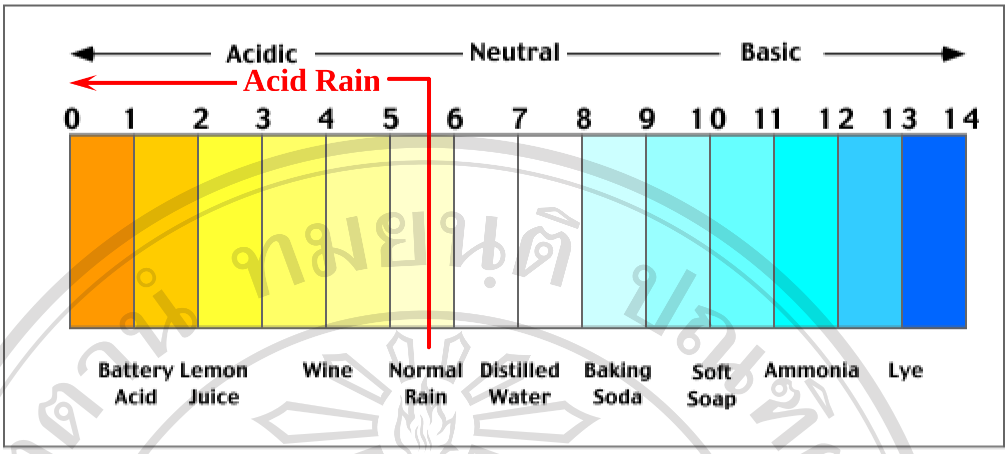

Figure 1.1 pH scale - acid rain in comparison with other substances

(http://www.livinglandscapes.bc.ca)

1.4 Acid Deposition

Acid pollutants in atmosphere can be deposited from atmosphere to the earth in several forms. The precise term to describe this process is "acid deposition". It can be separated into two forms which are wet and dry depositions. Wet deposition is commonly well known as acid precipitation that can be found in many forms such as rain, snow, hail, fog and cloud vapor. Beside, Dry deposition is referring to an acidic gases and particle in atmosphere, which also can deposit to the earth.

Both of them can cause an environment damages. The wind can transfer acidic particle onto several kinds of receptor such as forest, lake, buildings, etc. Dry deposited gases and particles can also be washed from trees and other surfaces by rainstorms. When that happens, the runoff water adds those acids to the acid rain, making the combination more acidic than the falling rain alone (http://www.epa.gov). Dry deposition generally occurs close to the point of emission. Wet deposition, however, may occur thousands of kilometers away from the original source of emission.

Carbon dioxide gas in atmosphere forms carbonic acid with moisture and changes the pH of rainfall to perform weak acid. However, this mildly acidic rain doesn't cause damages to the environment. But when rain becomes more acidic than this, the problems has begun. The rain which has pH lower than 5.6 was started to be acid rain. It becomes more acidic due to the contamination of pollutants in atmosphere. The main primary pollutants, which can be cause of acid rain are SO_2 and oxide of nitrogen (NO_x).

1.4.1 Sulfur oxide

Sulfur containing compounds are normally found in atmosphere in many forms. The most sulfur compounds in atmosphere are sulfur dioxide (SO_2), hydrogen sulfite (H_2S) and sulfate (SO_4^{2-}) in aerosol form. Sulfur dioxide is the most important of sulfur compound because its effect to human and environment by react with moisture in air to form sulfuric acid (H_2SO_4). Also sulfate (SO_4^{2-}) is the main part of photochemical smog (Radojecvic, M. and Harrison, R.M., 1992). Sulfur dioxide is nonflammable, non-explosive and colorless gas that causes a taste and sensation at concentration from 0.3 to 1.0 ppm in atmosphere. At the concentration above 3.0 ppm the gas has a pungent, irritating odor (http://reports.eea.eu).

Various animal species, including humans respond to sulfur dioxide by bronchoconstriction, which may be assessed in terms of an increase in airway resistance. Sulfuric acid is much more potent irritant than sulfur dioxide. Therefore most studies deal with combined sulfurous materials rather than with SO_2 alone.

Analysis of numerous epidemiological studies clearly indicates an association between air pollution, as measured by the concentration of SO_2 accompanied by particulate matter and moisture, and health effects of varying severity. This is especially true for short-term exposure. The association between long-term exposure and chronic disease morbidity and mortality is not so clear. Typical concentration data and associated health effects are present in Table 1.2. As can be seen from these data, sulfur dioxide in combination with particulate matter and moisture is a potentially serious health hazard (Kenneth *et. al*., 1998).

Table 1.2 Effects of SO_2 at various concentrations (Kenneth *et. al*., 1998).

Concentration	**Effect**
0.037-0.092 ppm, annual mean	Accompanied by smoke at a concentration of 185 μg/m^3, increased frequency of respiratory symptoms and lung disease may occur.
0.11-0.19 ppm, 24-hr mean	With low particulate level, increased hospital admission of older persons for respiratory disease may occur. Increased metal corrosion.
0.19 ppm, 24-hr mean	With low particulate level, increased mortality may occur
0.25 ppm, 24-hr mean	Accompanied by smoke at a concentration of 750 μg/m^3, increased daily death rate may occur (British data); a sharp rise in illness rates
0.3 ppm, 8 hr	Some trees shoe injury
0.52 ppm, 24-hr average	Accompanied by particulate matter, increased mortality may occur.

Sulfur dioxide can be reacted with moisture in atmosphere to form sulfuric acid via formation of sulfur trioxide by photochemical or catalytic processes in atmosphere. Examples of these formations are shown in equation below. The oxides of sulfur in combination with particulate matter and moisture produce the most damaging effect attributed to atmosphere air pollution.

Atmospheric sulfur dioxide is oxidized to forming sulfuric acid. The chemical mechanisms are shown as follows:

$$SO_2 + H_2O \leftrightarrow HOSO_2$$

$$HOSO_2 + O_2 \leftrightarrow HO_2 + SO_3$$

$$SO_3 + H_2O \leftrightarrow H_2SO_4$$

In the present of water droplets, which can take the form of fogs, clouds, rain or hygroscopic aerosols, sulfur dioxide will dissolve opening the possibility of aqueous phase oxidation.

$$SO_2 + H_2O \leftrightarrow SO_2 \cdot H_2O$$

$$SO_2 \cdot H_2O \leftrightarrow HSO_3^- + H^+$$

$$HSO_3 \leftrightarrow SO_3^{2-} + H^+$$

The equilibriums above are sensitive to pH, and HSO_3^- is the predominant species over the range pH 2-7 (Kenneth *et. al.*, 1998).

Sulfuric acid that occurred from a reaction of sulfur dioxide (SO_2) and moisture in air can be react further with ammonia or ion salt such as sodium chloride (NaCl) from sea salt particles to sulfate (SO_4^{2-}).

$$H_2SO_4 + NaCl \rightarrow Na_2SO_4 + 2HCl$$

$$H_2SO_4 + 2NaCl \rightarrow Na_2SO_4 + 2HCl$$

Beside, sulfur dioxide (SO_2) in air can be rapidly changed to sulfate (SO_4^{2-}) by react with ammonia in moist condition.

$$SO_2 + 2NH_3 + H_2O + \frac{1}{2}O_2 \rightarrow (NH_4)_2SO_4$$

Finally, sulfuric acid (H_2SO_4) sulfate (SO_4^{2-}) and hydrochloric acid (HCl) from all reaction above are fall back to the earth during raining period and cause the acid condition of rainwater as acid rain (Canter, 1986).

The major natural sulfur emissions are as: dimethyl sulphide (DMS), which is produced by marine phytoplankton and oxidized to SO_2 in the atmosphere; hydrogen sulphide (H_2S) from decay processes in soil and vegetation; and SO_2 from volcanoes. These sources are now heavily out-weighted by human ones, principally fossil fuel combustion, as shown in Table 1.3

Some of the natural sources are highly erratic, even when summed over the globe. It has been estimated, for example, Japanese volcanoes generate an average of 1.5 Mt SO_2 each year, with the result that around 20% of the sulfur in Japanese precipitation is of volcanic origin (Colls, 1997).

Table 1.3 Natural and human sources of sulfur dioxide (Colls, 1997).

Source	Global emission (Mt S)*
Natural	
DMS (dimethylsulfur)	16
Soils and vegetation	2
Volcanoes	8
Total natural	26
Anthropogenic	
Biomass burning	3
Fossil fuel combustion	70
Total anthropogenic	73
Total	99

***Note;** the emission strengths are given as mass of sulfur (S), not sulfur dioxide.

1.4.2 Oxide of nitrogen

Oxide of nitrogen (NO_x) in ambient air is the general term used to describe the group of highly reactive gases that contain nitrogen and oxygen in varying amounts (NO, NO_2, and other oxides of nitrogen). It plays a major role in the formation of ozone in the atmosphere through a complex series of reactions with volatile organic compound (VOCs). However, their quite different physical properties, chemical affinities and environmental impacts, they are often lumped together. Combustion always produces a mixture of NO_2 and NO, although typically more than 90% of combustion NO_x production is in the form of NO.

The pollutant concern of oxide of nitogen are mostly considered to nitric oxide (NO) and nitrogen dioxide (NO_2). By the major proportion of emitted NO_x (as the sum of the two compounds is known) is in the form of NO, although most of the atmospheric burden is usually in the form of NO_2 (Harrison, 1996).

Nitric oxide is form in two distinct ways:

- Thermal NO is formed from reactions between the nitrogen and oxygen in the air. The reactions can be summarized by the Zeldovitch mechanism:

$$N + O_2 \rightarrow NO + O$$

$$N + O_2 \rightarrow NO + O$$

This is highly endothermic, so that thermal NO production is at a maximum in the highest-temperature regions of a combustion chamber.

- Fuel NO is formed from nitrogen in the fuel. Typically, fuel nitrogen contents are 0.5-1.5% in oil and coal, and rather less in gas.

Only a small proportion of the NO_2 found in the atmosphere was released from source in this form. The remainder has been created in the atmosphere as part of the same photochemical activity that is responsible fro ozone formation. The nitric oxide from fossil fuel combustion reacts with ozone

$$NO + O_3 \rightarrow NO_2 + O_2$$

During daylight, the NO_2 absorbs blue and UV radiation (<420 nm.) and decomposes back to NO and O_3, resulting in a photochemical equilibrium between the four gases. In rural areas, away from the NO sources, the NO_2 concentration is usually considerably higher than NO. In urban areas the O_3 become depleted and the balance moves in favor of NO. The production of ozone, which requires more complex cycles involving organic compounds and radical. (Colls,1997).

Nitrogen dioxide acts as an acute irritant and in equal concentrations is more injurious than NO. However, at concentrations found in the atmosphere NO_2 is only potentially irritating to chronic obstructive pulmonary disease (COPD). Table 1.4 summarizes of health effects of exposure to NO_2 at concentrations from 0.25 to 1 ppm (Kenneth *et. al*., 1998).

Table 1.5 shows the global distribution of NOx emissions. Although most of the direct emission will be as NO, the source strengths are givens as NO_2 equivalent since the entire NO is potential available for oxidation to NO_2. Within this global emissions total of about 150 Mt, the table shows that over 70% of the total released is due to human activities. Only one third of total emissions were from natural sources.

Table 1.4 Key human health effects of exposure to NO_2 (US. EPA., 1993).

Clinical studies	
NO_2 in ppm (Exposure Duration)	**Observed Effected**
0.2-0.3 (0.5-2.0 hr.)	Trend toward increased airway responsiveness to challenges in asthmatics. However, no significant effects observed by same or other investigators at NO_2 levels up to 4 ppm. Small (4-6%) decreases in FEV_1 or FVC in adult or adolescent asthmatics, in response to NO_2 alone.
0.3 (3.75 hr.)	Small decreases (5-9%) in FVC and FEV_1 in COPD patients with mild exercise. No effects seen by other investigators for COPD patients at 0.5-2.0 ppm NO_2
1.5-2.0 (2-3 hr.)	Increased airway responsiveness to bronchoconstrictor in health adults. However, effects not detected by other investigators at 2-4 ppm.
=2.0 (1-3 hr.)	Lung function changes (e.g., increased airway resistance) in healthy subjects. Effects not found by others at 2-4 ppm.

FEV_1 = Forced expiratory volume in 1 s.

FVC = Forced vital capacity

COPD = Chronic obstructive pulmonary disease

Table 1.5 Global emissions of NO_x by source type (Kenneth *et. al*., 1998).

Source category	**Source strength (kt NO_2 per year)**	**Percent of total (%)**
Surface sources		
Fuel combustion		
Coal	21,000	13.7
Oil	10,200	6.6
Gas	7,600	4.9
Transport	26,300	17.1
Industrial	4,000	2.6
Soil release	18,100	11.8
Biomass burning		
Savannah	10,200	6.6
Deforestation	6,900	4.5
Fuel wood	6,600	4.3
Agricultural refuse	13,100	8.5
Atmospheric sources		
NH_3 oxidation	10,200	6.6
Lightning	16,400	10.7
High-flying aircraft	1,000	0.7
NO_x from stratosphere	2,000	1.4
Total emission	153,600	100.0

1.4.3 Less contribution of acid substances

In addition, other acids gases or particles contaminating in atmosphere also affect to the pH of precipitation. In consideration, ammonia and chloride are important in determine the acidity of precipitation.

a) Ammonia

Ammonia is the major acid neutralizing in the atmosphere and plays an important role in the chemistry of acid rain. The major sources are animal wastes and the application of fertilizers. In the UK, animal wastes are estimated to contribute about 80% of total emissions, cattle being responsible for as much as 60%. Ammonia emissions have increased in the recent years with more intensive animal husbandry. For example, over Europe, NH_3 emissions from livestock increase by 50% between 1950 and 1980 the largest increases occurring in the Netherlands, where emissions have more than doubled (Mason, 1992).

Ammonia generally exists as an alkaline vapor with capacity to neutralize either sulfuric or nitric acid in the atmosphere. It is readily soluble in water, dissociating to form ammonium (NH_4^+) and hydroxyl ions (OH^-). Liljestrand and Morgan (1978) and Munger (1982) have suggest that the pH of precipitation is controlled by the interaction of ammonia and other bases (metal carbonates and oxides) with sulfuric and nitric acid, and the presence of ammonium has been found increase the pH of rain and snow.

While it is likely that ammonia can react and neutralize the acidity in precipitation, the potential adverse effects may not be alleviated, since the ammonium ion (NH_4^+) can acidify soil through biological processes. In addition, fertilizer applications may have an adverse impact on ground water, lakes, and streams, in scarce, it has been noted that acidification of soil can result from the application of nitrogen fertilizer. When the rain coming, rainwater run-off was move into bodies of water at lower elevations than the fields where fertilizers were originally applied can lower the pH of lake and streams (Bubenick, 1984).

b) Hydrogen chloride

Chlorine is found in polluted atmosphere as the element itself, chlorine or as hydrogen chloride and others chlorine containing form. It is a highly soluble and reactive gas and though of minor importance on a global or regional scale, it can significantly influence acid deposition close to sources. In Western Europe, coal combustion is the major source, accounting for about 65% of total emission, with waste incineration being perhaps the next largest contributor. In the UK, coal combustion is estimated to contribute 93% to emission of HCl and waste incineration 6%. The spatial distribution will depend not only on where and how much coal is burnt, but also on its chloride content, which can vary from less than 0.1% to more than 0.4%. The annual emissions from coal are 250-350 kt. In the absence of a detailed emissions inventory, it is not possible to make reasonable accurate estimates of HCl deposition (Mason, 1992).

The concentration of chlorine and its compounds in the air are usually quite low. Cholak (1952) reported the average chlorine concentration in average American communities in the range of 0.016 to 0.078 ppm, calculated as Cl^-. A similar compilation by Katz (1955) showed average values in five cities in the range of 0.033 to 0.095 ppm. A few analysis has been made for organic halides. The values generally found are less than 0.1 ppm. The principle effects of chlorine and its compounds are corrosion, by hydrogen chloride and salt nuclei; respiratory irritation from chlorine possibly more deep-seated respiratory effects from complex ammonium chloride and damage to vegetation from chlorine (Faith, 1972).

1.5 Further Trends of Emission

Rapid urbanization increased industrialization and rising energy use, mostly derived from fossil fuel combustion. The growth in energy demand in recent decades has particularly marked in rapidly industrializing countries and regions. Between 1990 and 1993 Asia's energy consumption grew by 6.2% per year, whilst the global energy consumption fell by 1%. The Asia-Pacific region accounted for 41% of world coal consumption in 1993 and large power plant are the greatest contributors to sulfur dioxide pollution in many developing country regions. Figure 1.2 shows the SO_2 emission at the same time of Europe, North America, and Asia. Emissions in Europe and North America have been decreasing whilst Asia is increased.

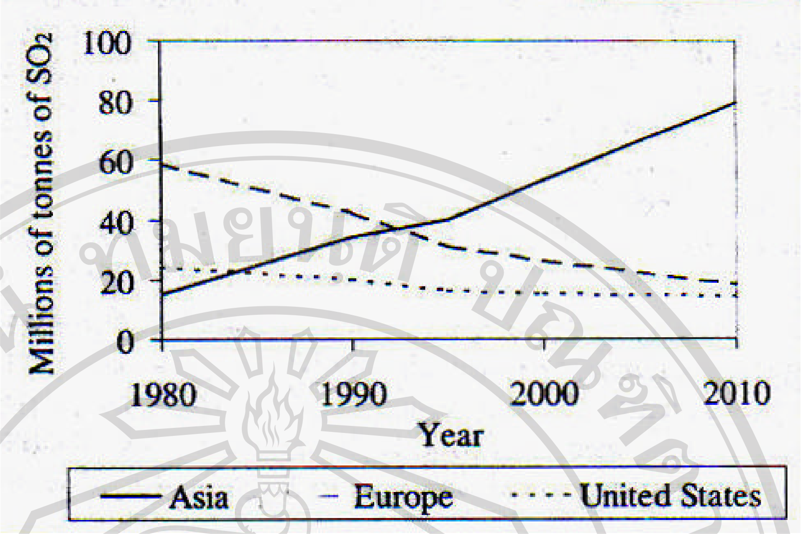

Figure 1.2 Regional SO_2 emissions from fossil fuel burning

(Hester and Harrison, 2002)

If developing countries follow a conventional development path, with the heavy reliance on coal and oil, with convergence of the use of control measures to 1995 levels by 2025, large increases in emissions of SO_2 and NO_x will result in some regions. As shown in Figure 1.3 and 1.4 the largest increase would be seen in China, South Asia and South East Asia (Hester and Harrison, 2002).

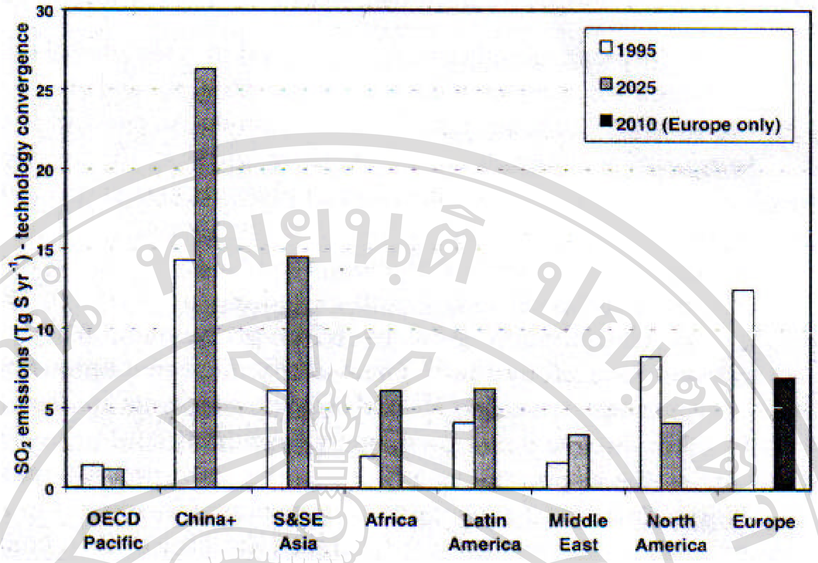

Figure 1.3 Anthropogenic SO_2 emissions from 1995 and projections for 2025 (Hester and Harrison, 2002)

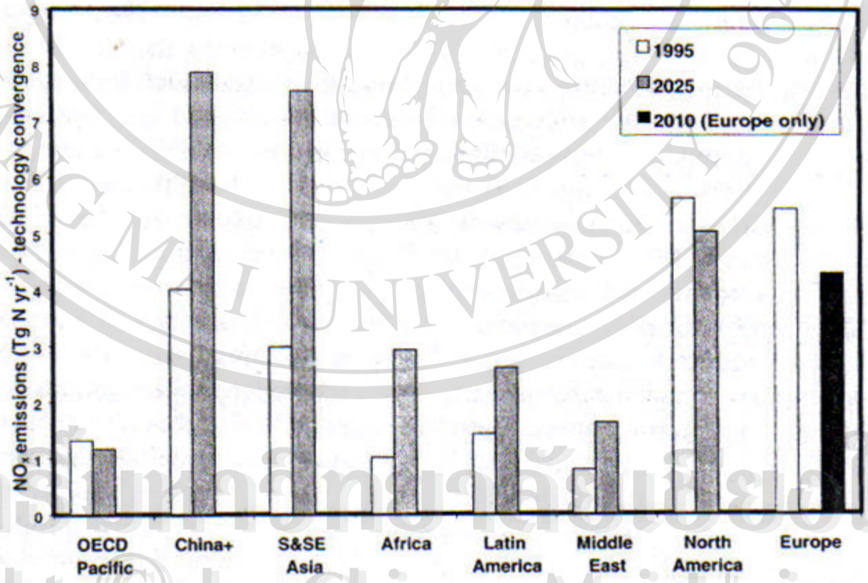

Figure 1.4 Anthropogenic NO_2 emissions from 1995 and projections for 2025 (Hester and Harrison, 2002)

1.6 Air pollution trends in Asia and the Pacific

The per capita commercial energy use more than doubled in most part of the Asia-Pacific region between 1975 and 1995. fossil fuels account for approximately 80% of energy generation in the region with both China and India relying heavily on coal, and this has resulted in rapidly increasing emissions of sulfur dioxide (at a rate at least four times higher than any other region between 1970 and 1986). NO_x emission from fossil fuel combustion has also increased (by about 70%). Primary, energy demand has grown in Asia over the last 25 years at a pace twice as fast as the world average (Shah *et al*., 2000), and the demand for coal and oil is expected to further double or triple in the next 30 years. Thus Asian sulfur emissions, already now nearly equal to those from Europe and North America combined (Foell *et al*., 1995), are expected to continue to increase in the next decades (Klimont *et al*., 2001).

Transportation contributes the largest share of air pollutant to the urban environment; urban levels of smoke and dust are generally twice the world average and more than five times as high as in industrial countries and Latin America (Hester and Harrison, 2002).

The rapid economic growth, increased energy demand and expansion of industries have made the Asian region increasingly exposed to emissions. Coal consumption which acts as the main process of energy production has generated large amount of acid precursors and has resulted in the acid deposition in some area of the world.

1.7 Transport and chemical transformation of acidifying gases

Since the pollutant gases emitted into the atmosphere, the pollutants are carried, dispersed, and diluted by atmospheric motions having a wide range of scales. The plume from a point source, such as power station, spreads out into an expanding cone, which meanders with fluctuations in the wind. For the most part, the plume is confined within the well-mixed atmospheric boundary layer, the depth of which may vary from a few hundred meters to about 2 km, depending on the time of day and the prevailing weather system. Ultimately, the plume will lose its coherence and shape as it becomes disrupted and distorted by convective motions and wind shear within the boundary layer. Within the mixing layer, emission plumes are dispersed both horizontally and vertically so that pollution concentration decreased steadily with distance downwind. Thus, by time a plume from a chimney 200 m high first contacts the ground some 10-20 km downwind, the concentration will be typically 10,000 times less than in the flue gas.

Beyond the point of contact with the ground, a good deal of the acidic pollutant is deposited on the surface or vegetation on dry (gaseous or particulate) form by absorption, impaction or sedimentation. The rest may travel for hundreds or even thousands of kilometers. During this travel time of up to the few days, the gases SO_2 and NO_x are oxidized and converted into sulfuric and nitric acid, either in gas-phase reactions or, more effectively, by being captured by cloud and raindrops (where the chemical transformations proceed much more rapidly in the liquid phase), and are eventually brought to the surface in rain or snow. These features are summarized in Figure 1.5

The rate of dry acid deposition is usually estimated by the product of the ground level concentration of the precursor gas (SO_2 or NO_x) and the ‘deposition velocity’. Measurements have shown that the deposition velocities vary from one surface to another (e.g. from bare soil to short grass to crops, etc.) and also depend on the stability of the air close to the ground, and therefore differ with time of day, weather, and season. For a typical deposition velocity of 0.8 cm/s, the amount of SO_2 uniformly mixed in the boundary layer 1 km deep wick be depleted by about 3% per hour. The actual flux or intensity of the dry acid deposition will decrease with increasing distance from the source, and how much remains to be deposited in this form depends on the extent to which the plume encounters cloud and rain and the rate at which the SO_2 is oxidized to sulfate during its travel (Mason, 1992)

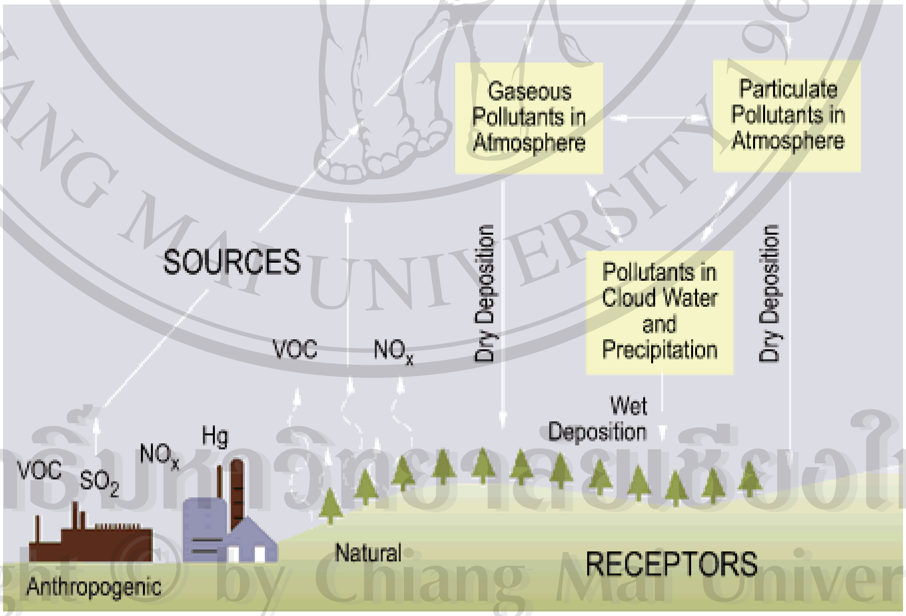

Figure 1.5 Mechanism of acidifying gases after emitted from sources. (http://www.epa.gov/airmarkets/acidrain/)

The rates of removal of sulfur from the atmosphere during rain are generally much greater than the rate of dry deposition. Moderate rain will often remove more material in one hour than will dry deposition over 2-3 days. However, the sulfur content of rainwater is far greater than can be accounted for by the dissolution of SO_2, which is limited by the fact that this increases the acidity of the water to a point where no more can dissolve. This self-limiting process allows only about 1% of atmospheric SO_2 to be removed in the way, and points to the necessity of the SO_2 being oxidized to sulfate before deposition (Mason, 1992).

1.8 Effect of acid deposition

Acid deposition is a global environment problem that affected many parts around the world not only in developing area, which is high emission of acidic pollutant. It affects to terrestrial, aquatic ecosystems, human health, etc. Details of its effect on each way are explains further in the following section.

1.8.1 Effect of acid deposition on terrestrial ecosystem

Before precipitation reaches the forest floor, its pH and chemical composition are altered as water drips through the forest canopy and runs over branches. In a mature forest, rain may wash through several layers of leaves before moved to the soil. The precipitation's pH, the intensity of the storm, the amount of dry deposits and the characteristics of the forest canopy all influence the extent of the chemical changes.

The toxic metals leached from the soils are very important to the welfare of green plants and the aquatic ecosystem. Through a series of chemical reactions, the important ions such as K^+, Ca^{2+}, Mg^{2+} and Na^+ are leached out and become unavailable to plant as nutrients.

Acid rain can also increase the weathering of silicate mineral in soils. This leads to a loss of mineral structure and possibly reduced fertility. However, not all soil is subject to the effects of acid rain. The vulnerable soils are those that are on glaciated areas of granite are other highly siliceous bedrock (granite, quartz and quartz sandstone), areas with which deposits of siliceous sands and areas of old and highly weathered and leached soils. Soils that are rich in lime are more resistant to acidity (because they are rich in calcium ions). In fact, lime is the best known buffer and consequently, is being used increasingly by farmers and foresters. Soils are less vulnerable to acid rain than surface water, because they have a buffering capacity. The buffering capacity depends mainly on the underlying bedrock and the human use and management of the soil (http://www.scar.utoronto.cal).

For example, Deciduous forest often less acidity (increase the pH) of precipitation moving through them by neutralizing hydrogen ions and releasing base-forming cations such as calcium (Ca^{2+}), magnesium (Mg^{2+}) and potassium (K^{+}). Most studies show that Coniferous forest vegetation is less able to neutralize acidic precipitation than deciduous forest vegetation (Voigt and May, 1989).

The cumulative effect means that even if the plant survives it will be very weak and unable to survive climatic conditions like strong winds, heavy rainfall, or a short dry period. Plant germination and reproduction is also inhibited by the effects of acid rain (http://ks.essortment.com).

1.8.2 Effect of acid deposition on aquatic ecosystem

After the acid rain moved down to the natural streams or reservoir, it will change the quality of water. The acid condition affected many aquatic organisms. Aquatic organisms have different tolerance of each species. Moreover, fish gradually disappear from these waterways as their environment slowly becomes intolerable. Some kinds of fish such as smallmouth bass, walleye, brook trout and salmon, are more sensitive to acidity than others and tend to disappear first. When the pH drops below 5.0, all the fish were died, and the bottom of the lake lies covered with un-decayed material as Table 1.6 shown the responded of organisms to decreasing of pH. Every year in temporate zone during the spring thaw, there is a sudden increase in the acidity of the lakes as frozen acid is suddenly deposited in them. This "Acid Shock." prevents the reproduction of aquatic species, or results in the deaths of the hatchlings.

Even those species that appear to be surviving may be suffering from acid stress in a number of different ways. One of the first signs of acid stress is the failure of females to spawn. Sometimes, even if the female is successful in spawning the hatchlings or fry are unable to survive in the highly acidic waters. This explains why some acidic lakes only have older fish in them (http://www.scar.utoronto.ca).

Table 1.6 Effects of an acidified ecosystem on the aquatic environment (http://www.ec.gc.ca/acidrain/).

As water pH approaches	**Effects**
6.0	• Crustaceans, insects, and some plankton species begin to disappear.
5.0	• Major changes in the makeup of the plankton community occur. • Less desirable species of mosses and plankton may begin to invade. • The progressive loss of some fish populations is likely, with the more highly valued species being generally the least tolerant of acidity.
Less than 5.0	• The water is largely devoid of fish. • The bottom is covered with un-decayed material. • The near shore areas may be dominated by mosses. • Terrestrial animals, dependent on aquatic ecosystems, are affected. Waterfowl, for example, depend on aquatic organisms for nourishment and nutrients. As these food sources are reduced or eliminated, the quality of habitat declines and the reproductive success of birds is affected.

Some acidified lakes are recovering, but many more are not. Of 202 lakes in Canada that have been studied since the early 1980s, 33% have reduced levels of acidity while 56% have shown no change and 11% have actually become more acidic.

The greatest improvements have been seen in the Sudbury area, where lakes had been very badly damaged. Here, fish populations have rebounded and fish-eating birds, such as loons, have increased. However, no substantial wildlife recovery has been seen beyond the Sudbury area. The least improvement has been seen in Atlantic Canada, even though lakes in this region were never as highly acidified as those in some parts of Ontario and Quebec. Since 1990, scientists have confirmed that maintaining lake's pH at 6.0 or more is the most appropriate criterion for calculating critical loads. This pH level encourages healthy aquatic systems in lakes, rivers and streams (http://www.ec.gc.ca).

1.8.3 Effected of acid deposition on human health

Sulfur dioxide affects to human health especially on respiratory system. The levels of harmful were varies on the concentration of pollutants in atmosphere and exposed time. The respond rates are also depends on each person.

As research into the acid deposition phenomenon has been studies, it has become evident that it has the potential to affect human health. These effects are not only by acid precipitation but also by acidic aerosols (particularly sulfates and nitrates). These substances can affect human health both directly (through contact with the skin, eyes and respiratory system) and indirectly. However, at ambient levels of acidity even in North America and Europe, very little direct damage has been observed expect through the inhalation of acidic aerosols, particularly sulfate. Asthmatics, those with other respiratory aliments, the elder and children are particularly susceptible to these direct impacts, which can result in decreased lung function, increased susceptibility to colds and allergies, bronchitis, and eventually in obstructive lung disease.

Indirect effects of acid deposition on human health may be potential more serious. These impacts include contamination of drinking water supplies (acid deposition can liberate toxic metal from the soil and water supply systems), and mercury and toxic metal poisoning through ingestion of fish from acidic waters and crops grown in acidic soils. Although the potential exist for such human health damage due to acid deposition, few effects have yet been observe at ambient levels even in the most polluted areas of North America and Europe (Bhatti *et al*., 1990)

1.8.4 Other effects of Acid deposition

All living things, living on land or in the water, are affected either directly or indirectly by acid rain. Even buildings, bridges and other structures are affected. In cities, paint from buildings have peeled off and colures of cars have faded due to the effects of acid rain. From the Taj Mahal in India to the Washington Monument great buildings all over the world have been affected by the acid rainfall which causes corrosion, fracturing, and discoloration in the structures. In Europe, structures like The Acropolis in Greece and Renaissance buildings in Italy, as well as several churches and cathedrals have suffered visible damage. In the Yucatan peninsula in Mexico, and in places in South America, ancient Mayan Pyramids are being destroyed by the acid rain. Temples, murals, and ancient inscriptions which had previously survived for centuries are now showing severe signs of corrosion. Even books, manuscripts, paintings, and sculpture are being affected in museums and libraries, where the ventilation system cannot eliminate the acid particles from the air which circulates in the building. In some parts of Poland, trains are required to run slowly, as the tracks are badly damaged due to corrosion caused by acid rainfall (http://ks.essortment.com).

1.9 Acid deposition monitoring program in Thailand

Since year 1992, Thailand had an experience about harmful of acid deposition due to SO_2 emitted from the Mae Moh lignite-fired power plant in Lampang province. Therefore Thai government was starting to reduce the acid deposition problems. In 1998, Thai government set up an acid deposition monitoring network in Thailand to monitor the situation and trend of acid deposition around country. By the corporation of related government agencies with the experts from university to perform and setup the method to measure wet and dry deposition. Also Thai government is joining with other Asian country to establish the Acid Deposition Monitoring Network in East Asia aimed to observe and solve this problem in the region. This network monitors an acidic pollutant in both, wet and dry form to assess the risk of its effect and changing on ecosystem. The monitoring stations are spread out to many part of our country and the government still has plan to set up more stations in the future.

The monitoring stations are located in various places such as in the city, industrial area, national park, etc. Data from each station are used to evaluate the acid deposition situation in that area. The change and trends of harmful cause from acid deposition also assess from these data (http://www.pcd.go.th).

The sampling point of this work is one of meteorological station belong to Faculty of Agriculture, Chiang Mai University. Site selection was followed the criteria of Acid Deposition Monitoring Network in East Asia (EANET). It was classified as the rural site which in the area of Mea Hia sub district. Its location was in The Mae Hia Research Center, Chiang Mai University Campus about 5 km. From the main campus of the university

1.10 Monitoring site

In general, a deposition monitoring site should not be located in areas dominated by local emission and contamination sources. Therefore, the selection of monitoring site should be given to minimize influences. Site should be selected in areas where monitoring can be continued over long period, and where land use in the vicinity is likely to remain in almost the same condition for decades. A deposition monitoring site also should not be located in areas dominated by local meteorological conditions. Therefore the study site was selected and installed in the area of Meteorological station, Mae-Hia Research Center, Chiang Mai University Campus which located in south west of Chiang Mai city.

The local criteria for placement of collectors in rural sites were followed the EANET guideline (EANET, 2000). Collector must be installed in open area which is far enough from trees, hills and other obstruction to avoid effects on sampling. The horizontal distance between a large obstruction and the collector at least twice the obstruction height, or the top of an obstruction as viewed from the collector should be less than 30° above the horizon. The collector must be free from local emission and contamination sources such as waste disposal sites, incinerators, parking lots open storage of agricultural products, and domestic heating. The horizontal distance between collector and rain gauge and dry deposition collector was greater than 2 meters. The rain gauge and the wet deposition collector were cross the direction of the prevailing wind during precipitation events.

Guidelines for Acid Deposition Monitoring in East Asia recommended that wet deposition monitoring site should be carried out at the same site used for dry deposition monitoring.

1.11 Wet deposition (EANET, 2000)

1.11.1 Monitoring frequency

Samples should be collected every 24 hours in principle. Collection can also be conducted for each precipitation event, but this is operationally inconvenient because site operators often find difficulty in determining the start and end of precipitation events, and because operator are not easily available to collect samples at all times of day and night. If a collection bucket is used, it should be changed everyday-whether precipitation occurred or not. The starting time of a day should be at 9.00 local time as a general rule. If a refrigerator is not in use, biocide should be used for preserving the samples.

1.11.2 Precipitation monitoring parameter

pH, electro-conductivity (EC) and concentration of ionic species (Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}) should be measured as required parameters.

1.11.3 Meteorological measurement

Wind speed/ direction, temperature, humidity precipitation amount and solar radiation to wet deposition should be measured on-site or at the nearest meteorological station in accordance with the measurement frequencies and methods of the meteorological monitoring system of each country.

1.11.4 Wet sample collection

All collected samples in this case refer to wet-only samples such as rain, hale, snow, etc. An automatic precipitation collector basically consists of a collecting bucket or funnel, a lid that can be opened and closed a precipitation sensor and a sample container. The operation of collector was also set up by the EANET criteria. The collector container or funnel opens automatically within 1 minute of onset of precipitation and close promptly at the end of the precipitation event.

a) The sensor has a minimum detection capability of 0.05 mm/h rainfall intensity and of 0.5 mm raindrop diameter, regardless of its direction.

b) The wet sample must shield from contamination by dry deposition.

c) The collector bucket or funnel with bottle used chemically inert to major constituents in acid precipitation. For container, polyethylene used as generally employed.

d) The height of the collection bucket is 1.0 - 1.5 m from the ground.

The capacity of containers should be considered from the maximum precipitation amounts of each time. The other details of sampling condition have to collect as sample documentation was containing;

- Sample identification number
- Sample start date, start time, end date and end time.
- Standard rain gauge precipitation depth reading.
- Sample contamination
- Instrument condition

- Site condition
- Operator’s remarks

The standard operating procedures at sampling site must be check and maintenance of the precipitation chemistry collectors and standard gauge, etc. Typical operations include the checking for proper sensor response and heating, hood movement, cleaning of the collection funnel and standard rain gauge funnel (used De-ionize water which conductivity less than 0.15 ms/m).

Some contaminants as microorganism are known to induce changes in the concentration of ammonium, nitrate and organic acids in the rain samples. To avoid this effect refrigeration should be done after measurement of sample volume. If sample volume is more than 200 ml the part of the sample in excess of 200 ml can be discharged. The samples were stored in polyethylene bottles and kept refrigerator at 4°C. Samples were shipped to analytical laboratory with in weekly or biweekly for the case of 24 hours collected sample and monthly for weekly-collected samples.

1.11.5 Data control and data reporting

This section is part of quality assurance and quality control of all results. There are three propose concerning quality assurance of data control.

1) Assure that all sample data will be stored in database in a data control.
2) Mark with flags that data whose accuracy and representation are doubted.
3) Recognize and describe samples that were measured without standard methods, i.e. with contamination, instrument trouble, bulk sampling, etc.

a) Data reporting

The data of wet deposition analysis were reported in two groups of data.

1) Site information, shipping, laboratory operation, chemical analysis, etc.

2) Measurement results of precipitation chemistry including precipitation amounts, calculated index. Remark and note also compose major part of the measurement results.

b) Quality assurance/ Quality control (QA/QC)

I) Accuracy of chemical analysis

The artificial precipitations were sent from a reference laboratory. In this study, two samples of artificial precipitation were distributed by Pollution Control Department of Thailand. Their code numbers were 031 and 032 for high and low ion concentration, respectively. The analytical results were used to calculate ion and conductivity balance in order to check the accuracy of analysis.

II) Cation and anion balance (R1)

The principle of electro-neutrality in precipitation water requires that total anion equivalents equal total cation equivalents. The ion balance values are control by required criteria as show in Table 1.8. According to this principle ion balance in a precipitation samples should be check by the following equation:

$$R_1 = [(C - A)/(C + A)] \times 100\%$$

Where C and A represents anion and cation equivalent, respectively

This is simplified from of the corresponding equation use by US EPA where the denominator is the average of the two sums.

$$A(\mu eq/L) \quad = \quad SC_{Ai} \times V_i$$

Where C_{Ai} is the concentration of i-th anion in µmol/L, V_i is the valence of the given ion.

$$C(\mu eq/L) \quad = \quad 10^{(6-pH)}/1.008 + S\ C_{ci} \times V_i$$

Where C_{ci} is the concentration of i-th cation in µmol/L. If the unit mg/L is used, it should be converted as follows:

$$(\mu mol/L) \quad = \quad (mg/L) \times 1000 / M$$

where the molecular weight (M) for cations and anions is given in Table 1.7

When pH is grater than 6 and R1 is significantly greater than zero, bicarbonate (HCO_3^-) concentration should be included for the computation of R1 and R2. when formic acid, acetic acid, or both are measured, formate and acetate ions should be considerd in the evaluation of R1 and R2. The concentrations (µeq/L) of these weak acids will be calculated from the discussion constant, K_a and pH as follows:

$$\left[HCO_3^-\right] = P_{CO_2} H_{CO_2} K_{a1} / \left[H^+\right] \qquad = \left(360\times10^{-6}\right)\left(3.4\times10^{-2}\right)10^{pH-6.35+6}$$

$$= 1.24\times10^{pH-5.35}$$

$$\left[HCOO-\right] = \left[HCOOH\right]Ka / \left[H+\right] \qquad = \left[HCOOH\right]\times10^{pH-pKa}$$

$$= \left[HCOOH\right]\times10^{pH-3.55}$$

$$\left[CH_2COO^-\right] = \left[CH_3COOH\right]Ka / \left[H^+\right] \qquad = \left[CH_3COOH\right]\times10^{pH-pKa}$$

$$= \left[CH_3COOH\right]\times10^{pH-4.56}$$

Constants for HCO_3^-, $HCOO^-$, CH_3COO^- are included in Table 1.7.

Table 1.7 Basic constants of each ion (EANET, 2000)

Ion	**Molecular weight (M)**	**Molar conductivity (?) S cm^2/mol**
H^+	1.008	349.7
NH_4^+	18.04	73.5
Ca^{2+}	40.08	59.8 x 2
K^+	39.10	73.5
Mg^{2+}	24.31	53.3 x 2
Na^+	22.99	50.1
NO_3^-	62.01	71.5
SO_4^{2-}	96.06	80.0 x 2
Cl^-	35.45	76.3
HCO_3^-	61.02	44.5
$HCOO^-$	45.00	54.6
CH_3COO^-	59.10	40.9
F^-	19.00	55.5
Br^-	79.90	78.2
NO_2^-	46.01	71.8
PO_4^{3-}	94.97	69.0 x 3

Table 1.8 Required criteria for R_1 (EANET., 2000)

(C+A), µeq/L	R_1, %
< 50	± 30
50-100	± 15
> 100	± 8

III) Comparison between Calculation and Measurement in Electric conductivity (R2)

For dilution solutions (e.g. below 10^{-3} M), the total conductivity can be calculated in mS/m from the molar concentrations and molar conductivity (at infinity dilution) of the individual ions. The calculation is as follows:

$$\Lambda_{\text{calc}} = \sum c_i \, \Lambda_i^0 \times 10^{-4}$$

Where ?$_{\text{calc}}$ denotes the calculated conductivity of the solution (in mS/m), Ci the ionic concentration of the i-th ion (in µmol/L), ?$_{i}^{0}$ the molar conductivity (in S cm^2/mol) at infinite dilution and 25 °C.

Thus

$$\Lambda calc = \left\{ \begin{array}{l} 349.7\times10^{(6-pH)} + 80.0\times2c\left(SO_4{}^{2-}\right) + 71.5c\left(NO_3{}^{-}\right) + 76.3c\left(Cl^{-}\right) \\ +73.5c\left(NH_4{}^{+}\right) + 50.1\left(Na^{+}\right) + 73.5c\left(K^{+}\right) + 59.8\times2c\left(Ca^{2+}\right) + 53.3\times2c\left(Mg^{2+}\right) \end{array} \right\} /1000$$

Where c(...) denotes the ionic concentrations in µmol/L of the ion in parentheses and the constants are the molar conductivity of the individual ion at infinite dilution at 25 °C (Table 1.7).

The calculation conductivity values can then be compared to the observed value for precipitation samples as the relation below

$$R_2 = \left(\left(\Lambda_{calc} - \Lambda_{meas} \right) / \left(\Lambda_{calc} + \Lambda_{meas} \right) \right) \times 100\%$$

This is similar to the equation for the calculation of cation and anion balance.

The required comparison criteria of measured and calculated conductivities are expressed in Table 1.9. If the required conductivity comparison criteria have not been met, the analysis should be repeated or a flag should be entered into the database indicating that the resulted did not meet the required criteria.

Table 1.9 Required criteria for R_2 (EANET., 2000)

? $_{meas}$, mS/m	**R_2, %**
< 0.5	± 20
0.5-3	± 13
> 3	± 9

1.12 Dry deposition (EANET, 2003).

1.12.1 Monitoring frequency

The Guideline describes that weekly data are expected and daily data are also accepted in the case of ion concentrations to be measured by filter pack. The monitoring frequency of the filter pack method should follow these descriptions fundamentally. If weekly sampling is difficult to be carried out, biweekly sampling could also be acceptable. It is desirable that the sampling is carried out through a year continuously. If is difficult, adequate sampling duration in every month should be determined.

1.12.2 Precipitation monitoring parameter

The analytical parameters of dry deposition were as same as parameters of wet deposition. However, the pH and Electric-conductivity were not measured.

1.12.3 Specification of filters

a) Filters for aerosol sampling; F0

Aerosols were collected at the first stage. The first stage filter was mounted in front of the other filters collecting gases. The material of the aerosol filter should not absorb acid and alkali gases and should have acceptable efficiency to collect sub-micron particles because sulfate aerosols are mostly of the fraction below 1 µm. For this purpose, PTFE (Polytetrafluoro eythlene) filter was preferred.

b) Filters for nitric acid sampling; F1

The second stage filter is designated to collect nitric acid (HNO_3). HNO_3 passes through the first stage and trapped on the second filter in principle. In order to collect HNO_3 separately from other nitrogen oxides, Nylon (polyamide) filter was preferred. It has to be taken notice that the second polyamide filter collects partial sulfur dioxide, hydrochloric acid and ammonia as along with nitric acid from the sampling air.

c) Filters for sulfur dioxide and hydrochloric acid samplings; F2

The remaining sulfur dioxide and hydrochloric acid that pass through the second stage will be collect on the third stage. The remaining sulfur dioxide and hydrochloric acid react with alkali substance on the filter mounted on the third stage. For this purpose, cellulose filters impregnated by potassium carbonate are preferred.

For the calculations of ambient concentrations, the amounts of sulfur dioxide, hydrochloric acid, and ammonia collected by the second filter to be added to those collected by alkali-impregnated filters.

d) Filter for ammonia sampling; F3

The remaining ammonia that passes through the second and third stage will be collected on the fourth stage. The remaining ammonia reacts with acid substance on the fourth stage. The filters are preferable to be impregnated by phosphoric acid. In this case, cellulose filters which are same as the third stage filters could be utilized.

For the calculation of ambient concentration, the amount of ammonia collected by the second filter has to be added to that collected by the acid-impregnated filters. The specifications are summarized in Table 1.10

Table 1.10 Specifications and reaction of four stage filter pack (EANET, 2003)

Stage	**Specification on filter**	**Reaction**	**Collected species**
1st(F0)	Polyetetrafluoro ethylene filter (PTFE), pore size 0.8 mm, diameter 47 mm.	Filtration	Aerosols
2nd(F1)	Polyamine filter, pore size 0.45 mm, diameter 47 mm.	Absorption and neutralization by collected acid gas	HNO_3, partial SO_2, partial HCl, NH_3
3rd(F2)	Impregnated filter; 6% K_2CO_3 + 2% glycerin on cellulose acetate filter pore size 0.45 mm, diameter 47 mm.	Neutralization by alkali impregnated cellulose filter	SO_2 , HCl
4th(F3)	Impregnated filter; 5% H_3PO_4 + 2% glycerin, cellulose acetate filter pore size 0.45 mm, diameter 47 mm.	Neutralization by acid impregnated cellulose filter	NH_3

1.12.4 Determination of concentration

The results from filter pack were calculated to assess the concentration of acid pollutant in ambient air. The concentrations of compound in air are basically determined as follows:

$$C_{air} = a \times net\ C_{sol} \times V_{sol} / V_{air} \quad (a = 10^3 / M)$$

Where

C_{air} : Concentration in the air (nmol/m³)

$net\ C_{sol}$: Net concentration in the solution (mg/L)

V_{sol} : Volume of the solution (ml)

V_{air} : Volume of the sampled air corrected at 20°C (m^3)

M : Molecular weight (g)

The $net\ C_{sol}$ should be calculate by:

$$C_{sol} \quad = \quad C_{sol,\ sample} - C_{sol,\ blank\ ;}$$

Where

$C_{sol,\ sample}$: Concentration in the solution from the sample filter (mg/L)

$C_{sol,\ blank\ ;}$: Median concentration in the solution from the blank filter (mg/L)

Determinations of concentrations for all pollutant species were summarized in Table 1.11

Table 1.11 Equations for determinations of concentrations in ambient air (EANET, 2003)

Species	M	Equation
SO_4^{2-}	96.06	$C_{air} = \propto \times \text{net } C_{sol,\ F0} \times V_{sol} / V_{air}$
NO_3^-	62.01	
Cl^-	35.45	
Na^+	22.99	
K^+	39.10	
NH_4^+	18.04	
Ca^{2+}	40.08	
Mg^{2+}	24.31	
SO_2	96.06 (SO_4^{2-})	$C_{air} = \propto \times (\text{net } C_{sol,\ F1} + \text{net } C_{sol,\ F2}) \times V_{sol} / V_{air}$
HNO_3	62.01 (NO_3^-)	$C_{air} = \propto \times \text{net } C_{sol,\ F1} \times V_{sol} / V_{air}$
HCl	35.45 (Cl^-)	$C_{air} = \propto \times (\text{net } C_{sol,\ F1} + \text{net } C_{sol,\ F2}) \times V_{sol} / V_{air}$
NH_3	18.04 (NH_4^+)	$C_{air} = \propto \times (\text{net } C_{sol,\ F1} + \text{net } C_{sol,\ F3}) \times V_{sol} / V_{air}$

Note $a = 10^3 / M$

net $C_{sol,F0}$ = the net C_{sol} of the F0 sample filter

net $C_{sol,F1}$ = the net C_{sol} of the F1 sample filter

net $C_{sol,F2}$ = the net C_{sol} of the F2 sample filter

net $C_{sol,F3}$ = the net C_{sol} of the F3 sample filter

1.13 Geography and climate of Chiang Mai province

Chiang Mai is the Province in Northern part of Thailand which situated between north latitude 17-21 and east longitude 98-99. Chiang Mai valley is 310 meters (1,027 feet) above sea level, and its covers 20,170 square kilometers. The wide point of the province of Chiang Mai measured as 136 kilometers (85 miles) and the longest is 320 kilometers (200 miles). Figure 1.6 shows the connection of Chiang Mai to others provinces. The north part, a 227 kilometers (141.82 miles) stretch of mountains divides Chiang Mai northern districts of Fang and Mae Ai from Burma Chiang Tung (Shan) state. In certain areas, the Kok River also acts as a border between Chiang Mai and Burma. On the east, Chiang Mai is bordered by the Chiang Rai, Lampang and Lamphun Provinces.

The Mae Tuen River, Ream Mountain and Luang Mountain separate Chiang Mai South from the province of Tak. Some portions of Chiang Mai South also border the Lamphun Province. To the west, Chiang Mai is bordered by Mae Hong Son Province. Beside, Chiang Mai is the origin of many rivers and streams such as Ping River, Cham River, Mea Tang River, etc.

In the area 20,170.057 square kilometers or 12,566,910 rai of Chiang Mai Province, it was divided to 22 districts and 2 sub districts. The characters of this province were mostly found the mountains and plain on hillside, it covers 10,397,501 rai (84.74 % of all area). An agriculture area were estimated around 1,611,283 rai (12.82%) and 558,127 rai (4.44%) for other proposed. The population of Chiang Mai Province in year 2003 is 1,603,220 persons, the most density of population are in Meang District and follow by Fang, San-Sai, and Mae Rim, respectively (http://chiangmai.nso.go.th). The data from an Investment office in year 2001 were recorded the number of factories in Chiang Mai as 2,297 factories, Most of them are the Food Production, Garment factories, Wood, etc (http://www.investmentthailand.com).

Chiang Mai is received and effect from 2 monsoons every years. One is North East monsoon and the other one is South West monsoon. Figure 1.7 shows the mountain ranges and season wind flow pattern in Asia. Both of them are affected to the weather in this region. The general meteorology characters of this province are concluded from the meteorological data in the pass 30 years (1971-2000). These data were measured by the Northern Meteorological Center. The measuring station is located in the area of Chiang Mai International Airport on latitude 18° 47'N longitude 98° 59' E, at 312 meters above sea level. The annual average temperature is 26.6 ° C with the maximum of 36 °C and minimum of 14.1 °C. Three seasons were recognized in this area. The details of each season are explains as follows;

1. Summer; this season start from middle of February to middle of May. At the beginning of this season. The direction of monsoon is change from North East monsoon to South West direction. The weather is dry and highest temperature was found in 23 April 1960 at 39.6 °C.

2. Rainy; the rainy season start from middle of May to middle of October. The highest numbers of rainy times were found in this period because of the influence from South West monsoon.

3. Winter; winter normally start from middle of October until middle of February. The North East monsoon is the prevailing wind during this period. Since the North

East monsoon through this region in October, the weather was change to unstable condition with reduced of temperature and moisture in atmosphere. The temperature is decreases below 20 °C. The lowest temperature which was collected from this station is 3.7 °C on 2 January 1974.

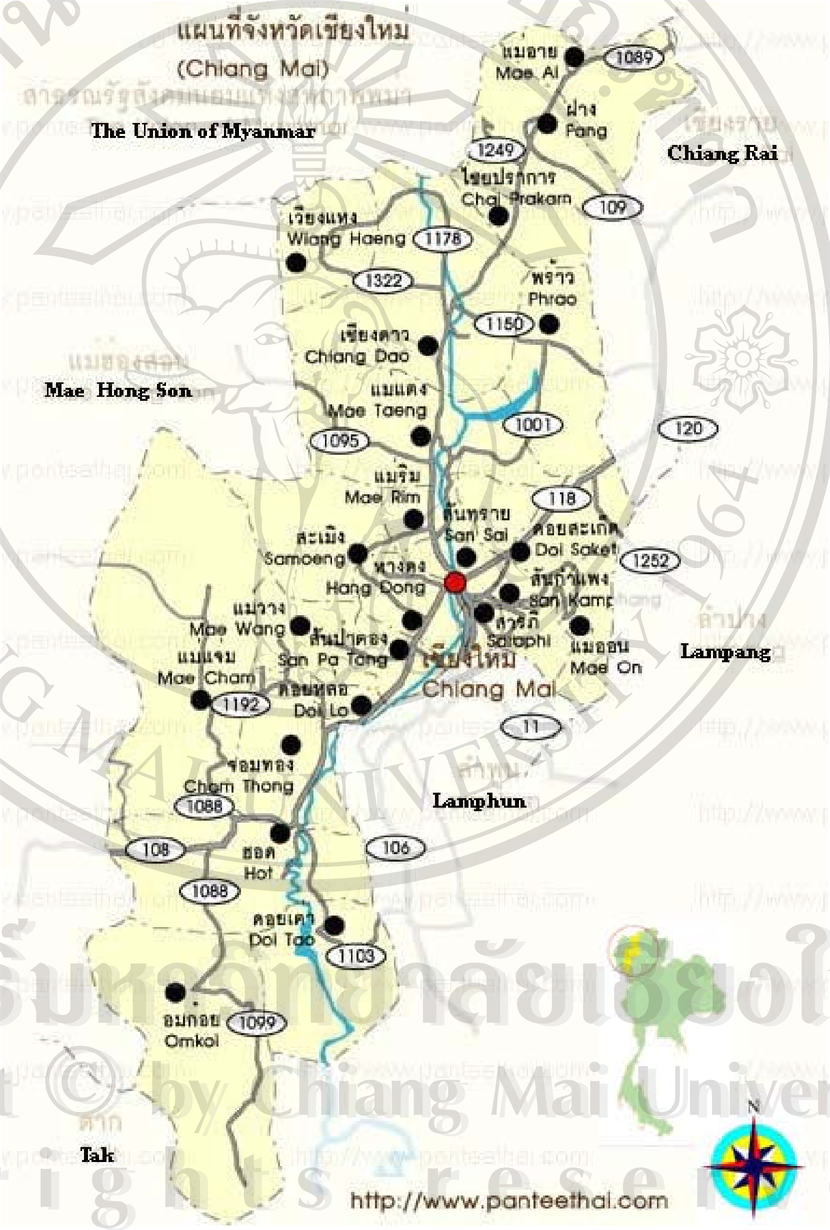

Figure 1.6 Map of Chiang Mai Province (www.panteethai.com)

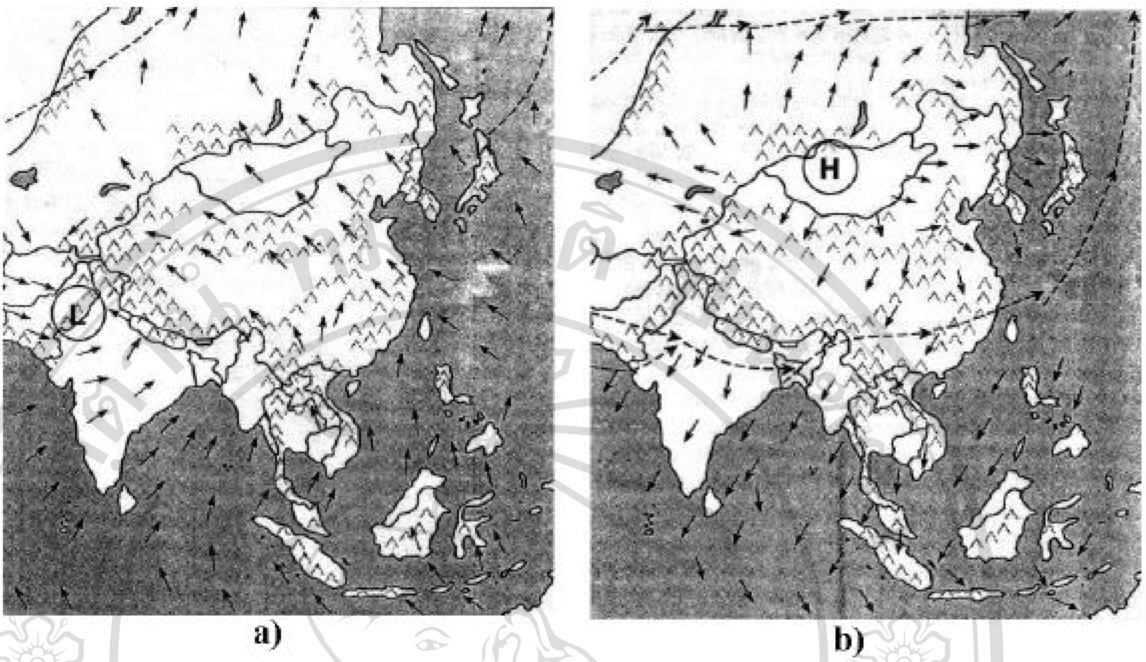

Figure 1.7 Mountain Range and wind flow pattern in Asia during summer (a) and winter (b) (Bhatti *et al*, 1990)

1.14 Ion chromatographic Method

Ion chromatography is a separation technique, which was developed for solving several specific analytical problems in aqueous systems. Small and his team first introduced the advance of ion chromatography in 1975, the low-capacity packed column and suppressor conductivity were employed for the first prototype IC by this group. The separation of ion chromatographic technique is based on an exchange of analyse ions with the counter ions to the fixed ions of the ion exchanger. A copolymer, which is employed as the supporting material of ion exchanger, is usually synthesized with polystyrene and divinylbenzene. The various ionic species can be separated on the basis of the different affinities to functional group on stationary phase. The eluent or mobile phase is an aqueous solution of inorganic salt and often contains an organic solvent. The eluent performs a duty as the competing ion to the eluent analyse ion. The eluent power depends on the type of competing ion which is influenced by its charge, size, molecular weight (MW) and concentration. However, the separation is the result of all conditions of the ion chromatographic system.

The basic component of ion chromatographic system are the eluent containers for the mobile phase (reservoir), an eluent delivery system or pump(s) to move the eluent and sample through the system, an injection to allow sample introduction, a column(s) to provide solute separation, a suppressor to reduce the background conductivity, a conductivity detector to detect the separated components, a data collection or recorder to assist in interpretation and storage of results. The schematic diagram of ion chromatograph is shown in Figure 1.8

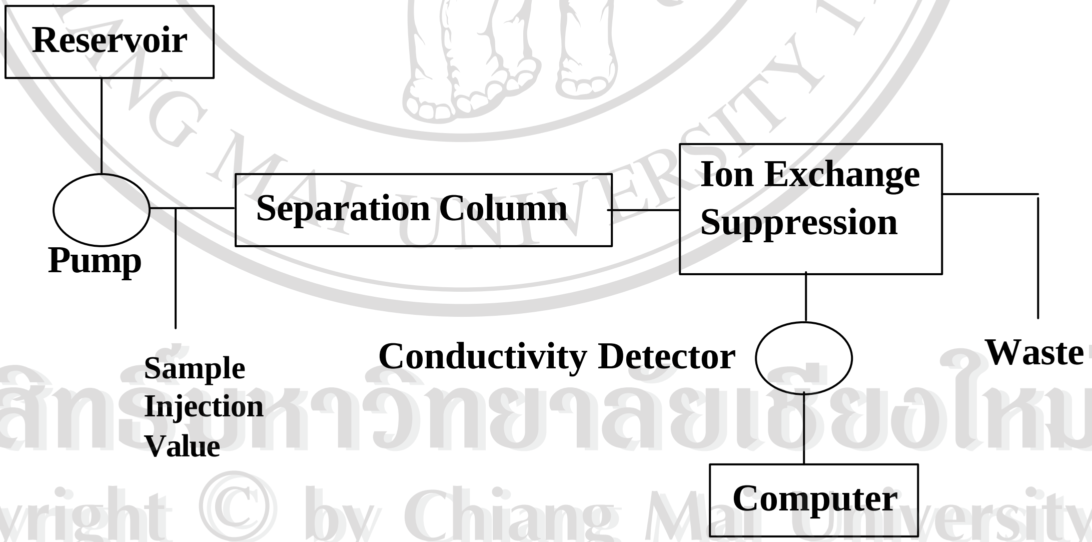

Figure 1.8 Components of ion chromatography with suppression system

1.15 Research Objectives

1. To monitor acid deposition in Chiang Mai Province.
2. To analyse acid deposition samples both in forms of wet and dry depositions.
3. To prepare database for control and reduce effects of acid deposition on environment and human health.