CHAPTER 1

INTRODUCTION

1.1 Introduction of acid deposition

Acid deposition or well known in the term of acid rain that is a broad term referring to a mixture of wet and dry deposition (deposited material) from the atmosphere containing higher than normal amounts of nitric and sulfuric acids. The precursors, or chemical forerunners, of acid rain formation result from both natural sources, such as volcanoes and decaying vegetation, and man-made sources, primarily emissions of sulfur dioxide (SO_2) and nitrogen oxides (NO_x) resulting from fossil fuel combustion. Acid rain occurs when these gases react in the atmosphere with water, oxygen, and other chemicals to form various acidic compounds. The result is a mild solution of sulfuric acid and nitric acid. When sulfur dioxide and nitrogen oxides are released from power plants and other sources, prevailing winds blow these compounds across state and national borders, sometimes over hundreds of miles.

Acid rain was first reported in Manchester, England, which was an important city during the industrial revolution. An English chemist, Augus Smith, working in Manchester as an early UK Inspector of Factories in the 1850s, was apparently the first to analyze in a systematic way the chemistry of rain near the industrial heartland of Britain. The term “acid rain” was used for the first time by him in 1872 (Cowling, 1980; Seinfeld and Pandis, 1998). The problem of acid rain is hence not a new one but the nature of the problem has changed from being a local problem for towns and cities to being an international problem. In Smith’s time, acid rain fell both in towns pollutants can be transported thousands of kilometers before washed out due to the introduction of tall chimneys dispersing pollutants high into the atmosphere.

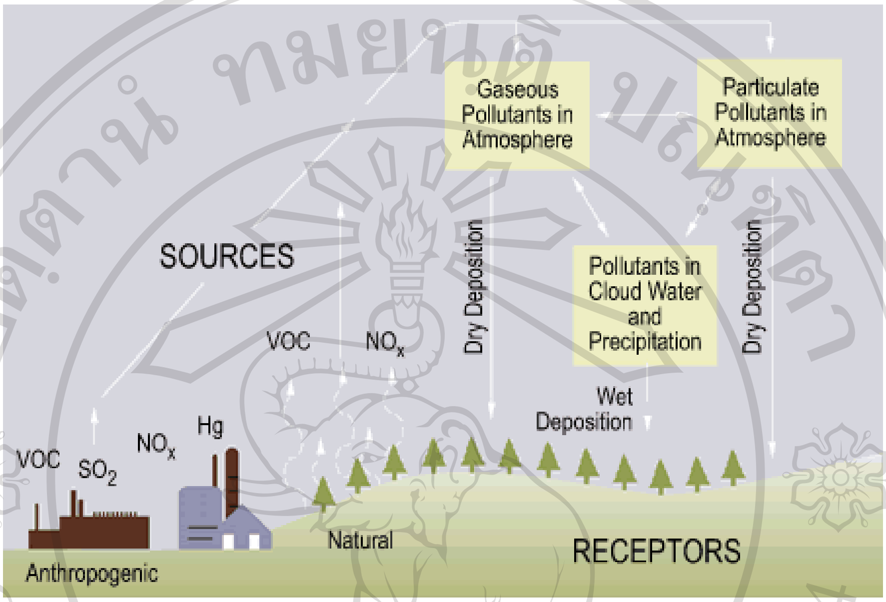


Figure1.1 The process of acid deposition (EPA, 2002)

1.1.1 Wet deposition

Wet deposition refers to acid rain, fog and snow. If acid chemical in the air are blown into areas where the weather is wet, the acids can fall to the ground in the form of rain, snow, fog, or mist. As this acidic water flows over and through the ground, it affects a variety of plants and animals. The strength of the effects depends on several factors, including how acidic the water is; the chemistry and buffering capacity of the soils involved; and the types of fish, trees, and other living things that rely on the water.

1.1.2 Dry deposition

The area where whether is dry, the acid chemical may became interoperated into dust or smoke and fall to the ground through dry deposition, sticking to the ground, buildings, homes, cars, and trees. Dry deposited gases and particles can be washed from these surfaces by rainstorms, leading to increased runoff. This runoff water makes the resulting mixture more acidic. About half of the acidity in the atmosphere falls back to earth through dry deposition.

1.2 Acidic pollutants

Actually, precipitation is naturally acidic because of carbon dioxide and water (20 degree Celsius at atmospheric pressure) in the air react together to from carbonic acid has a slightly acidic pH of 5.6. Therefore, rainfall that has pH less than 5.6 may be considered as acid rain. The most important gasses which lead to acidification are sulfur dioxide (SO_2), nitrogen oxides (NO_x) and hydrogen chloride (HCl).

1.2.1 Sulfur dioxide, SO_2

Sulfur dioxide is a colorless, non-flammable, non-explosive gas. This gas released as a byproduct of combusted fossil fuels containing sulfur. A variety of industrial processes, such as the production of iron and steel, utility factories, and crude oil processing produce this gas (e.g. reaction 1.1, 1.2 and 1.3).

Sulfur dioxide is obtained by burning sulfur;

$$S\,(s) + O_2\,(g) \rightarrow SO_2\,(g) \qquad (1.1)$$

Roasting pyrite (iron sulfide) or other metal sulfides prior to smelting;

$$4\,FeS\,(s) + 7\,O_2\,(g) \rightarrow 2\,Fe_2O_3\,(s) + 4\,SO_2\,(g) \qquad (1.2)$$

Burning hydrogen sulfide from crude oil;

$$2\,H_2S\,(g) + 3\,O_2\,(g) \rightarrow 2\,SO_2\,(g) + 2\,H_2O\,(g) \qquad (1.3)$$

After being released into the atmosphere, sulfur dioxide can either be deposited on the Earth's surface in the form of dry deposition or goes through several complex steps of chemical reactions before they become the acids found in acid rain. The steps are broken down into two phases, gas phase (photo-oxidation) which would produce a high oxidation rate during the middle of the day and aqueous phase oxidation which be independent of sunlight (Spedding, 1974; Mason, 1992). The rate at which oxidized determines its lifetime in the atmosphere provided that oxidation is the most important removal mechanism. A number of field experiments have been carried out to give the SO_2 oxidation rates summarized in Table 1.1.

Table 1.1 Summary of SO_2 oxidation rate studies in the atmosphere (Sedding, 1974)

Source of SO_2	Concentration of SO_2 on release from source (mg kg^{-1})	Relative humidity during measurement	Rate of SO_2 consumption in atmosphere (% ks^{-1})
Ni smelter	0.1 – 1.0	-	0.6
Smelter	0.01 – 20.3	65-70%	190
Coal-fired power plant	2200	70-100%	1.7
Coal-fired power plant	2200	100%	8.3

There are various potential reactions that can contribute to the oxidation of sulfur dioxide in the atmosphere each having varying degrees of success. One is photo-oxidation of sulfur dioxide by means of ultraviolet light. This process uses light form of the electromagnetic spectrum. The reactions are shown below;

$$OH\bullet + SO_2 \rightarrow HO.\,SO_2 \text{ adduct } (+ O_2, H_2O) \rightarrow H_2SO_4\,(aq) \qquad (1.4)$$

The gas phase oxidation of sulfur dioxide (reaction (1.4)) represents several steps. The rate-determining step is shown in reaction (1.4), and forms the $HO.SO_2$ adduct, which OH radical resulting from the photolytic decomposition of ozone and reaction with water vapor, i.e.

$$O_3 + hv \rightarrow O\bullet + O_2 \qquad (1.5)$$

$$O\bullet + H_2O \rightarrow 2HO\bullet \qquad (1.6)$$

The adduct reacts rapidly with O_2 to form SO_3 which in turn reacts with vapory water to form sulfuric acid aerosols (Castleman et al., 1975; Viggiano and Arnold, 1983; Khoder, 2002; Sanderson *et al*., 2006). On the other hand, Wang *et al*. (1988) found that the reaction of SO_3 and vapory water is quite slow in the gas phase. A second and more common process is belonging to aqueous phase oxidation. The steps of reaction (Spedding, 1974; Sanderson *et al*., 2006) are shown below.

$$SO_2\,(g) + H_2O \longleftrightarrow SO_2\,(aq) \qquad (1.7)$$

$$SO_2\,(aq) + H_2O \longleftrightarrow H_2SO_3\,(aq) \qquad (1.8)$$

$$H_2SO_3(aq) + H_2O \longleftrightarrow HSO_3^- + H_3O^+ \qquad (1.9)$$

SO_2 reacts with moisture found in the atmosphere; SO_2 immediately oxidizes to form a sulfite and bisulfite ion, respectively. Afterwards, it becomes sulfuric acid by two main routes depending on the SO_2 concentration. At low SO_2 concentrations found in remote areas, the bisulfite is oxidized by hydrogen peroxide, i.e.

$$HSO_3^- + H_2O_2 \longleftrightarrow HSO_4^- + H_2O \qquad (1.10)$$

In more polluted regions, where the concentration of SO_2 is higher, the peroxide supply is inadequate. The oxidation by ozone becomes significant (Monn and Schaeppi, 1993; Colls, 2002). They added that SO_2 can be converted directly to H_2SO_4 after reaction with the OH radical. Beside, sulfur dioxide (SO_2) in air can be rapidly changed to sulfate (SO_4^{2-}) by react with ammonia in moist condition.

$$2SO_2 + 4NH_3 + 2H_2O + O_2 \rightarrow 2(NH_4)_2SO_4 \qquad (1.11)$$

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).

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 SO2 alone. Analysis of numerous epidemiological studies clearly indicates an association between air pollution, as measured by the concentration of SO2 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 SO2 at various concentrations (Kenneth *et. al*., 1998).

Concentration Effect	**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/m3, 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.

1.2.2 Oxide of nitrogen, NOx

The other chemical that is also chiefly responsible for the make-up of acid rain is nitrogen oxides (NO_x). Oxides of nitrogen is a term used to describe any compound of nitrogen with any amount of oxygen atoms (Table 1.2). By the major proportion of emitted NO_x is in the form of nitrogen monoxide or NO and nitrogen dioxide or NO_2 which most of the atmospheric burden is usually in this form (Harrison, 1996). Theses gasses are byproducts of firing processes of extreme high temperatures (automobiles, utility plants), and in chemical industries (fertilizer production) that some reactions are shown below. Natural processes such as bacterial action in soil, forest fires, volcanic action, and lightning make up five percent of nitrogen oxide emission. Transportation makes up 43 percent, and 32 percent belongs to industrial combustion (http://www.geocities.com).

Table 1.3 Oxides of nitrogen (Spedding, 1974)

Oxide	Formation	Stability in the atmosphere
Dinitrogen oxide	N_2O	Stable gas
Nitrogen oxide	NO	Stable gas
Dinitrogen trioxide	N_2O_3	Unstable gas $N_2O_3 \longleftrightarrow NO + NO_2$
Nitrogen dioxide	NO_2	Stable gas
Dinitrogen tetroxide	N_2O_4	Unstable gas $N_2O_4 \longleftrightarrow 2\,NO_2$
Dinitrogen pentoxide	N_2O_5	Unstable gas $N_2O_5 \longleftrightarrow N_2O_3 + O_2$
Nitrogen trioxide	NO_3	Unstable gas (never isolated)

Nitrogen oxides rise into the atmosphere and are oxidized in clouds to form nitric or nitrous acid. These reactions are catalyzed in heavily polluted clouds where traces of iron, manganese, ammonia, and hydrogen peroxide are present. Nitrogen oxides rise into the atmosphere mainly from automobile exhaust. In the atmosphere it reacts with water to form nitric or nitrous acid follow the reaction (1.11) below.

$$2NO_2\,(g) + H_2O\,(l) \longrightarrow HNO_3\,(aq) + HNO_2\,(aq) \qquad (1.12)$$

Richards (1983) and Russell *et al*. (1986) suggested that there are two different mechanisms for the formation of nitric acid which operate in the day and night. In the daytime, hydroxyl radical appears to be predominantly (reaction 1.13) whilst at night, N_2O_5 hydrolysis (reaction 1.14 to 1.16) is an important source of HNO_3 (Russell *et al*., 1986, Rodhe *et al*., 1988).

$$NO_2 + OH\bullet + M \longrightarrow HNO_3 + M \qquad (1.13)$$

$$NO_2 + O_3 \longrightarrow NO_3^- + O_2 \qquad (1.14)$$

$$NO_3^- + NO_2 \longleftrightarrow N_2O_5 \qquad (1.15)$$

$$N_2O_5 + H_2O \longrightarrow 2HNO_3 \qquad (1.16)$$

In reaction 1.12 becomes much less important at night because the hydroxyl radical is primary formed photochemically. At night, ozone will reacts with NO_2 to form NO_3, which rapidly reacts with NO_2 to form N_2O_5. The N_2O_5 will react with water in droplets in the atmosphere and then convert to nitric acid. Richard (1983) suggested that this pathway is unimportant in the daytime because N_2O_5 is in equilibrium with NO_3^-, which is photolyzed as well as rapidly destroyed to NO. This reaction (1.17) is shown below.

$$NO_2 + h\nu \longrightarrow NO + O \qquad (1.17)$$

The NO_2 absorbs strongly in ultraviolet region, dissociating to NO and atomic oxygen. Consequently, N_2O_5 in reaction 1.15 (daytime) is less than in nighttime.

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 NO_x 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 FEV1 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 FEV1 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.

FEV1 = Forced expiratory volume in 1 s.

FVC = Forced vital capacity

COPD = Chronic obstructive pulmonary disease

Table 1.5 Global emissions of NOx 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
Fuel wood	6,600	4.5
Agricultural refuse	13,100	4.3
Deforestation	6,900	8.5
Atmospheric sources		
NH_3 oxidation	10,200	6.6
Lightning	16,400	10.7
High-flying aircraft	1,000	0.7
NOx from stratosphere	2,000	1.4
Total emission	153,600	100.0

1.2.3 Hydrogen chloride, HCl

A third acidic pollutant associated with some fossil fuels and other industrial activities is hydrogen chloride or HCl. This is a highly soluble and reactive gas. In Western Europe, coal combustion is the major source, accounting for about 65 percent of total emissions being perhaps the next largest contributor. In the UK, coal combustion is estimated to contribute 93 percent to emissions of HCl.

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).

1.3 Sources of ions in rainwater

Most rainwater has a pH of 5.6 to 5.8, simply due to the presences of carbonic acid (H_2CO_3). The latter is formed from dissolved CO_2 gas and H_2O. The source of the CO_2 is the atmosphere, which presently contains about 380 ppm CO_2.

$$CO_2\,(g) + H_2O \longleftrightarrow H_2CO_3\,(l) \quad (1.18)$$

$$H_2CO_3 \longleftrightarrow H^+ + HCO_3^- \quad (1.19)$$

If values of pH below 5.6 or above, it will show that something interferes in rainwater. As far as rain in concerned, abnormal acidity or bacidity is relative to CO_2-

H_2O equilibrium values of 5.6 to 5.8. There are both natural and non-natural sources of materials that cause rain pH to deviate from the CO_2-H_2O equilibrium values.

The rainwater has pH more than 5.8 because it has interacted with a basic substance at some point in their history. Probably this was in the soils or rocks. The most common one is calcium carbonate ($CaCO_3$). Calcium carbonate may be present as limestone or marble. Another possibility is the closely related material $Ca(Mg)CO_3$ (dolomite), which is calcium carbonate with some magnesium impurity in it. A second common base found in soils of either agricultural or heavily forested areas in ammonia (NH_3). Either of these bases may be the cause of the high pH. But the rain waters have pH less than 5.6 because they have interacted with acidic substance like SO_2 and NO_x to form strong acid (H_2SO_4 and HNO_3). Some ions and sources of ions that contain in rainwater are shown in Table 1.3.

Table 1.6 Sources of ions in rainwater (Berner, and Berner, 1987; Canter, 1986)

Ion	Origin		
	Marine Input	Terrestrial Input	Pollution Inputs
Na^+	Sea Salt	Soil Dust	Burning Vegetation
Mg^{2+}	Sea Salt	Soil Dust	Burning Vegetation
K^+	Sea Salt	Biogenic aerosols, Soil Dust	Burning Vegetation, Fertilizer
Ca^{2+}	Sea Salt	Soil Dust	Manufacture of Cement, Burning of Fossil Fuels

Table 1.6 (continued**)**

Ion	Origin		
	Marine Input	Terrestrial Input	Pollution Inputs
Cl^-	Sea Salt	Volcanism	Industrial Cl^- chemicals, Gas Release, Road Salt
SO_4^{2-}	Sea Salt	H_2S from Decay	Burning of Fossil Fuels, Marine Gases
NO_3^-	-	Lightning, Decay of Organic Matter	Auto and Truck Emissions, Burning of Fossil Fuels
NH_4^+	-	NH_3 from Bacterial Decay	Ammonia Fertilizer, Decomposition of Sewage, Combustion
$HCOO^-$	-	Photochemical Reaction, insects	Vegetation , ants
CH_3COO^-	-	Photochemical Reaction, insects	Vegetation , ants
PO_4^{3-}	-	Soil Dust, Biogenic Aerosols, Absorbed on Sea Salt	Fertilizers, Burning Vegetation
SiO_2, Al^{3+}, Fe^{3+}	-	Soil Dust	Land Clearing

1.4 Measuring 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.

$$pH = -\log[H^+]$$

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.

Acid rain is measured using a scale called “pH.” The lower a substance's pH, the more acidic it is. The pH scale is used to measure the acidity or alkalinity of an aqueous solution and is determined by the hydrogen ion (H^+) content. Pure water has a pH of 7.0. However, normal rain is slightly acidic because carbon dioxide (CO_2) dissolves into it forming weak carbonic acid, giving the resulting mixture a pH of approximately 5.6 at typical atmospheric concentrations of CO_2. This scale was invented by a Danish scientist, Sorenson, in 1909. A pH from 6.5 to 8 is considered the safe zone. Between these numbers, organisms are in very little or no harm. Figure 1.2 shows pH scale.

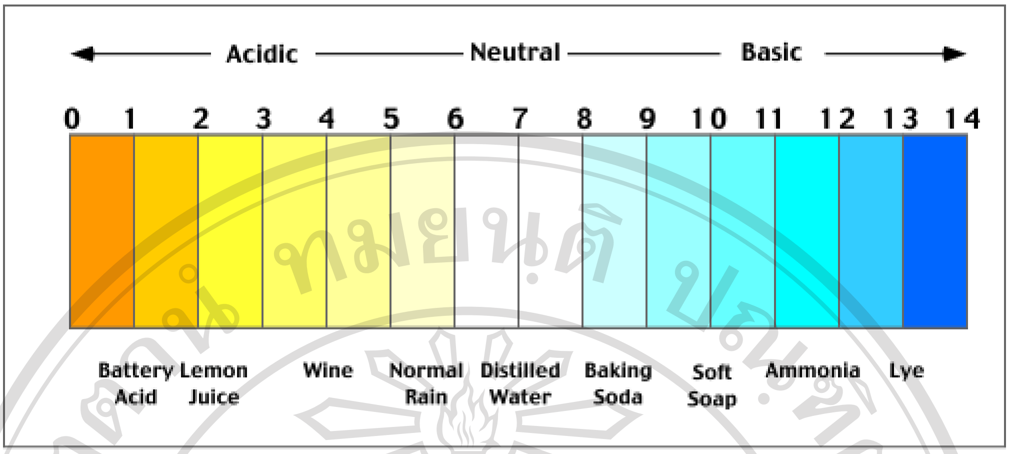


Figure 1.2 pH scales (www.physicalgeography.net/fundamentals/8h.html)

The pH scale is logarithmic rather than linear (see Figure 1.3), and so there is a ten fold increase in acidity with each pH unit, such that rainfall with pH 5 is ten times more acidic than pH 6, rainfall with pH 4 is 100 times more acidic than pH 6 and rainfall with pH 3 is 1000 times more acidic than pH 6.

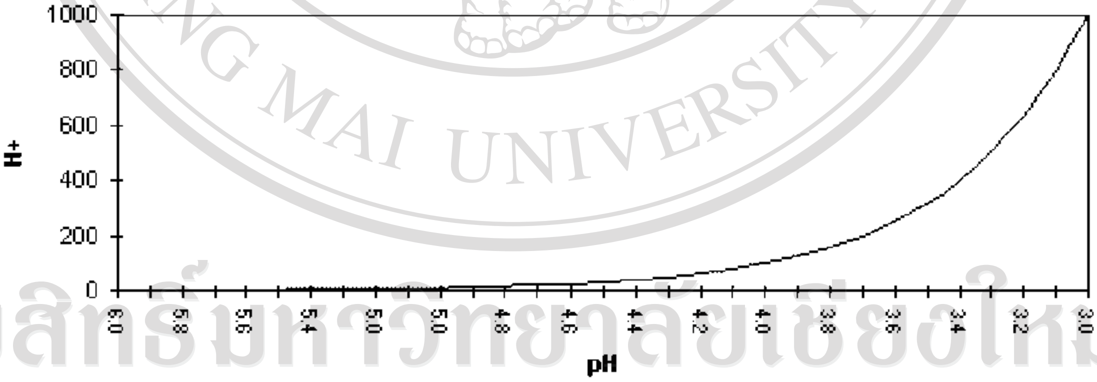


Figure 1.3 The logarithmic pH scale for range pH 6.0 - pH 3.0 (http://www.ace.mmu.ac.uk/)

Rainfall acidity is measured in pH units. The individual pH readings may be converted to hydrogen ions to give a linear rather than a logarithmic representation of acidity. To convert the pH values to hydrogen ions, the following formula applies;

$$H^+ (\mu eq/L) = \ln (6.0 - pH) \qquad (1.20)$$

Where; H^+ (μeq/L) is the hydrogen ion content in micro equivalents per liter (a unit which measures the concentration of hydrogen ions in a liter of water).

The hydrogen ion content of various pH values is given in the Table 1.4 and illustrated on Figure 1.2

Table 1.7 Correlations between pH value and H^+ (http://www. ace.mmu.ac.uk/)

pH value	H^+ (μeq/L)	pH value	H^+ (μeq/L)
6.0	< 1	4.0	100
5.5	3	3.5	316
5.0	10	3.0	1000
4.5	32	2.5	3162

1.5 Effects of acid deposition

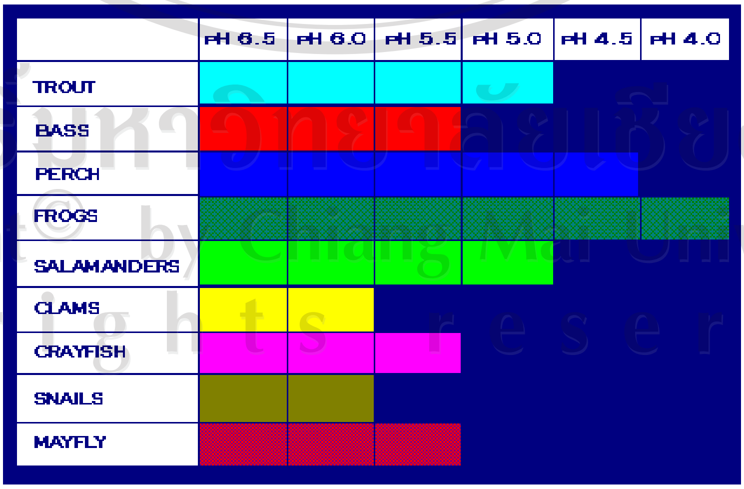
Acid rain causes acidification of lakes and streams and contributes to the damage of trees at high elevations (for example, red spruce trees above 2,000 feet) and many sensitive forest soils. In addition, acid rain accelerates the decay of building materials and paints, including irreplaceable buildings, statues, and sculptures that are part of our nation's cultural heritage. Prior to falling to the earth, sulfur dioxide (SO_2) and nitrogen oxide (NO_x) gases and their particulate matter derivatives—sulfates and nitrates—contribute to visibility degradation and harm public health.

1.5.1 Effects of acid deposition on aquatic ecosystems

The ecological effects of acid deposition are most clearly seen in the aquatic, or water, environments, such as streams, lakes, and marshes. Acid deposition flows into streams, lakes, and marshes after falling on forests, fields, buildings, and roads. Acid deposition also falls directly on aquatic habitats. Most lakes and streams have a pH between 6 and 8, although some lakes are naturally acidic even without the effects of acid deposition. Acid deposition primarily affects sensitive bodies of water, which are located in watersheds whose soils have a limited ability to neutralize acidic compounds (called “buffering capacity”). Lakes and streams become acidic (i.e., the pH value goes down) when the water itself and its surrounding soil cannot buffer the acid rain enough to neutralize it. In areas where buffering capacity is low, acid rain releases aluminum from soils into lakes and streams; aluminum is highly toxic to many species of aquatic organisms.

Many lakes and streams examined in a National Surface Water Survey (NSWS) suffer from chronic acidity, a condition in which water has a constant low pH level. The survey investigated the effects of acidic deposition in over 1,000 lakes larger than 10 acres and in thousands of miles of streams believed to be sensitive to acidification. Of the lakes and streams surveyed, acid rain caused acidity in 75 percent of the acidic lakes and about 50 percent of the acidic streams. Several regions in the U.S. were identified as containing many of the surface waters sensitive to acidification. They include the Adirondacks and Catskill Mountains in New York state, the mid-Appalachian highlands along the east coast, the upper Midwest, and mountainous areas of the Western United States.

Acid rain causes a cascade of effects that harm or kill individual fish, reduce fish population numbers, completely eliminate fish species from a water body, and decrease biodiversity. As acid rain flows through soils in a watershed, aluminum is released from soils into the lakes and streams located in that watershed. So, as pH in a lake or stream decreases, aluminum levels increase. Both low pH and increased aluminum levels are directly toxic to fish. In addition, low pH and increased aluminum levels cause chronic stress that may not kill individual fish, but leads to lower body weight and smaller size and makes fish less able to compete for food and habitat. Some types of plants and animals are able to tolerate acidic waters. Others, however, are acid-sensitive and will be lost as the pH declines. Generally, the young of most species are more sensitive to environmental conditions than adults. At pH 5, most fish eggs cannot hatch. At lower pH levels, some adult fish die. Some acid lakes have no fish. The figure 1.2 shows that not all fish, shellfish, or the insects that they eat can tolerate the same amount of acid; for example, frogs can tolerate water that is more acidic (i.e., has a lower pH) than trout.



	pH 6.5	pH 6.0	pH 5.5	pH 5.0	pH 4.5	pH 4.0
TROUT	🟦	🟦	🟦	🟦		
BASS	🟥	🟥	🟥			
PERCH	🟦	🟦	🟦	🟦	🟦	
FROGS	🟩	🟩	🟩	🟩	🟩	🟩
SALAMANDERS	🟩	🟩	🟩	🟩		
CLAMS	🟨	🟨				
CRAYFISH	🟪	🟪	🟪			
SNAILS	🟫	🟫				
MAYFLY	🟥	🟥	🟥			

Figure 1.4 Acidic toleration scales of some organisms in the water (www.epa.gov)

1.5.2 Effects of acid deposition on terrestrial ecosystems

Over the years, scientists, foresters, and others have noted a slowed growth of some forests. Leaves and needles turn brown and fall off when they should be green and healthy. In extreme cases, individual trees or entire areas of the forest simply die off without an obvious reason. After much analysis, researchers now know that acid rain causes slower growth, injury, or death of forests. Acid deposition has been implicated in forest and soil degradation in many areas such as the Shenandoah and Great Smoky Mountain National Parks of the eastern U.S. Of course, acid deposition is not the only cause of such conditions. Other factors contribute to the overall stress of these areas, including air pollutants, insects, disease, drought, or very cold weather. In most cases, in fact, the impacts of acid deposition on trees are due to the combined effects of acid deposition and these other environmental stressors. After many years of collecting information on the chemistry and biology of forests, researchers are beginning to understand how acid rain works on the forest soil, trees, and other plants.

A spring shower in the forest washes leaves and falls through the trees to the forest floor below. Some trickles over the ground and runs into streams, rivers, or lakes, and some of the water soaks into the soil. That soil may neutralize some or all of the acidity of the acid rainwater. This ability is called buffering capacity, and without it, soils become more acidic. Differences in soil buffering capacity are an important reason why some areas that receive acid rain show a lot of damage, while other areas that receive about the same amount of acid deposition do not appear to be harmed at all. The ability of forest soils to resist, or buffer, acidity depends on the thickness and composition of the soil, as well as the type of bedrock beneath the forest floor. Midwestern states like Nebraska and Indiana have soils that are well buffered. Places in the mountainous northeast, like New York's Adirondack and Catskill Mountains, have thin soils with low buffering capacity.

Acid deposition does not usually kill trees directly. Instead, it is more likely to weaken trees by damaging their leaves, limiting the nutrients available to them, or exposing them to toxic substances slowly released from the soil. Quite often, injury or death of trees is a result of these effects of acid deposition in combination with one or more additional threats. Scientists know that acidic water dissolves the nutrients and helpful minerals in the soil and then washes them away before trees and other plants can use them to grow. At the same time, acid deposition causes the release of substances that are toxic to trees and plants, such as aluminum, into the soil. Scientists believe that this combination of loss of soil nutrients and increase of toxic aluminum may be one way that acid rain harms trees. Such substances also wash away in the runoff and are carried into streams, rivers, and lakes. More of these substances are released from the soil when the rainfall is more acidic.

However, trees can be damaged by acid deposition even if the soil is well buffered. Forests in high mountain regions often are exposed to greater amounts of acid than other forests because they tend to be surrounded by acidic clouds and fog that are more acidic than rainfall. Scientists believe that when leaves are frequently bathed in this acid fog, essential nutrients in their leaves and needles are stripped away. This loss of nutrients in their foliage makes trees more susceptible to damage by other environmental factors, particularly cold winter weather.

1.5.3 Effects of acid deposition on human health

Acid deposition looks, feels, and tastes just like clean rain. The harm to people from acid rain is not direct. Walking in acid deposition, or even swimming in an acid lake, is no more dangerous than walking or swimming in clean water. However, the pollutants that cause acid rain—sulfur dioxide (SO_2) and nitrogen oxides (NO_x)—do damage human health. These gases interact in the atmosphere to form fine sulfate and nitrate particles that can be transported long distances by winds and inhaled deep into people's lungs. Fine particles can also penetrate indoors. Many scientific studies have identified a relationship between elevated levels of fine particles and increased illness and premature death from heart and lung disorders, such as asthma and bronchitis.Based on health concerns, SO_2 and NO_x have historically been regulated under the Clean Air Act, including the Acid Rain Program.

1.5.4 Effects of acid deposition on materials

Acid rain and the dry deposition of acidic particles contribute to the corrosion of metals (such as bronze) and the deterioration of paint and stone (such as marble and limestone). These effects significantly reduce the societal value of buildings, bridges, cultural objects (such as statues, monuments, and tombstones), and cars. Dry deposition of acidic compounds can also dirty buildings and other structures, leading to increased maintenance costs. Chiang Mai University Campus about 5 km from the main campus of the university.

1.6 Acid deposition monitoring program in Thailand

Since year 1992, Thailand had an experience about harmful of acid deposition due to SO2 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.

1.7 Ion chromatography for analysis of acid deposition

Ion Chromatography (IC) was introduced in 1975 by Small, Stevens, and Bauman (Frank and Richard, 1983) as a new analytical method. Within a short period of time, ion chromatography evolved from a new detection scheme for a few selected inorganic anions and cations to a versatile analytical technique for ionic species in general. For a sensitive detection of ions via their electrical conductance, the separator column effluent was passed through a second column. This second column, "stripper", later called the "suppressor" column. This suppressor column chemically reduces the eluent background conductance, while at the same time increasing the electrical conductance of the analyte ions (Small *et al.*, 1975).

At the end of the 1970s, ion chromatographic techniques were used to analyze organic ions for the first time. The requirement for a quantitative analysis of organic acids brought about an ion chromatographic method based on the ion-exclusion process that was first described by Wheaton and Bauman in 1953. The 1980s witnessed the development of high efficiency separator columns with particle diameters between 5 µm and 8 µm, which resulted in a significant reduction of analysis time. In addition, separation methods based on the ion-pair process were introduced as an alternative to ion-exchange chromatography, because they allow the separation and determination of both anions and cations (Weiss, 2004).

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Today the chromatographic analysis of ionic materials is widely applied and rapidly expanding. The number of species that may be determined continues to grow, as does the number of areas of science and technology where IC plays an important role. Application of ion chromatography at the present time can be seen through type of sample such as acid rain, pharmaceuticals, pesticides, wastewater and drinking water (Small, 1989).

1.7.1 Ion chromatographic system (Weiss, 2004).

The basic components of an ion chromatograph are shown in Figure 1.9. It resembles the setup of conventional HPLC systems.

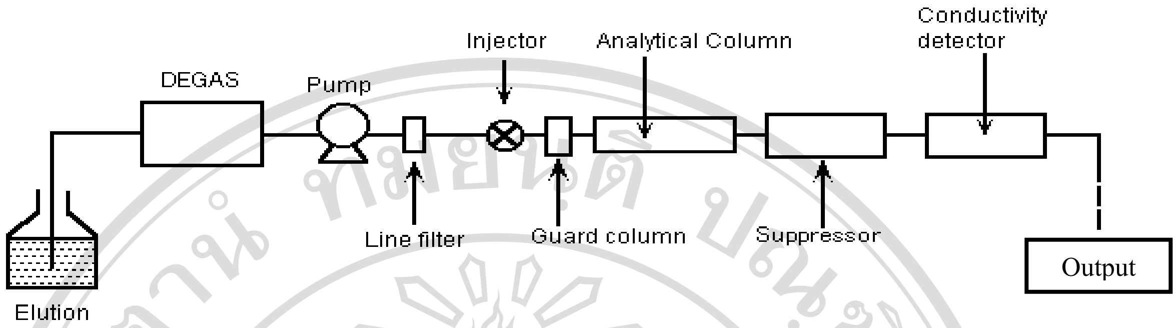

Figure 1.5 Basic components of an ion chromatograph

A pump delivers the mobile phase through the chromatographic system. In general, either single-piston or dual-piston pumps are employed. A pulse-free flow of the eluent is necessary for employing sensitive UV/Vis and amperometric detectors. Therefore, pulse dampers are used with single-piston pumps and a sophisticated electronic circuitry with dual-piston pumps. The sample is injected into the system via a loop injector, as schematically shown in Figure 2.7. A three-way valve is required, with two ports being connected to the sample loop. The sample loading is carried out at atmospheric pressure. After switching the injection valve, the sample is transported to the separator column by the mobile phase. Typical injection volumes are between 5 µL and 100 µL.

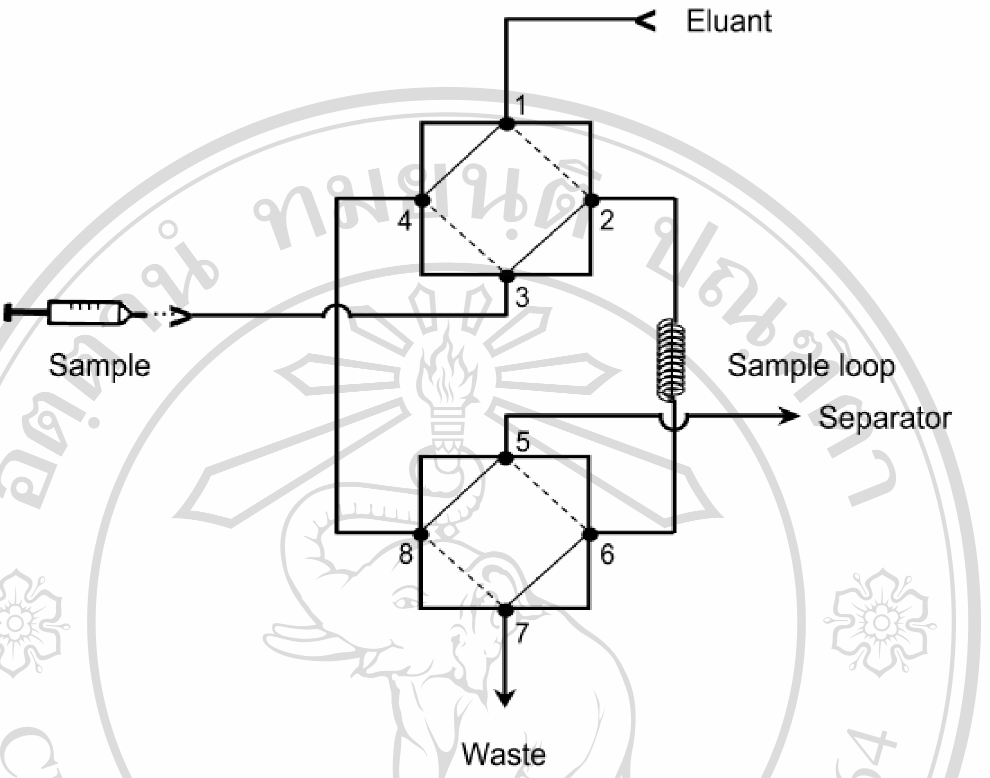

Figure 1.6 Schematic representation of a loop injector

The most important part of the chromatographic system is the separator column. The choice of a suitable stationary phase and the chromatographic conditions determine the quality of the analysis. The column tubes are manufactured from inert material such as Tefzec, epoxy resins, or PEEK (polyether ether ketone).

The analytes are detected and quantified by a detection system. The performance of any detector is evaluated according to the following criteria:

- Sensitivity
- Linearity
- Resolution (detector cell volume)
- Noise (detection limit)

The most commonly employed detector in ion chromatography is the conductivity detector, which is used with or without a suppressor system. The main function of the suppressor system as part of the detection unit is to chemically reduce the high background conductivity of the electrolytes in the eluent, and to convert the sample ions into a more conductive form. In addition to conductivity detectors, UV/Vis, amperometric, and fluorescence detectors are used.

The chromatographic signals can be displayed on a recorder. Quantitative results are obtained by evaluating peak areas or peak heights, both of which are proportional to the analyte concentration over a wide range. This was traditionally performed using digital integrators which are connected directly to the analog signal output of the detector. Due to low computer prices and lack of GLP/GLAP conformity, digital integrators are hardly used anymore. Modern detectors feature an additional parallel interface that enables the connection to a personal computer or a host computer with suitable chromatography software. Computers also take over control functions, thus allowing a fully automated operation of the chromatographic system.

Because corrosive eluents such as diluted acids and bases are often used in ion chromatography, all parts of the chromatographic system being exposed to these liquids should be made of inert, metal-free materials. Conventional HPLC systems with tubings and pump heads made of stainless steel are only partially suited for ion chromatography, because even stainless steel is eventually corroded by aggressive eluents. Considerable contamination problems would result, because metal ions exhibit a high affinity towards the stationary phase of ion exchangers, leading to a significant loss of separation efficiency. Moreover, metal parts in the chromatographic fluid path would make the analysis of orthophosphate, complexing agents, and transition metals more difficult.

The determination of ionic species in solution is a classical analytical problem with a variety of solutions. Whereas in the field of cation analysis both fast and sensitive analytical methods (AAS, ICP, polarography, and others) have been available for a long time, the lack of corresponding, highly sensitive methods for anion analysis is noteworthy. Conventional wet-chemical methods such as titration, photometry, gravimetry, turbidimetry, and colorimetry are all labor-intensive, time-consuming, and occasionally troublesome. In contrast, ion chromatography offers the following advantages;

- Speed
- Sensitivity
- Selectivity
- Simultaneous detection
- Stability of the separator columns

1.8 Data analysis

1.8.1 Neutralization of acidity

Neutralization is a chemical reaction in which a base reacts with an acid to create water and a salt. In chemical terms, neutralization results from the interaction of ions in the acid and base. This reaction can occur between organic and inorganic compounds, between two inorganic compounds, between two organic compounds, and by adding a base to an acid or vice versa.

The acidity (pH) of precipitation is determined by the relative proportion of acids and bases in solution or rainwater sample. Major ions typically present in rainwater are hydrogen (H^+), sodium (Na^+), ammonium (NH_4^+), potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), chloride (Cl^-), nitrate (NO_3^-), sulfate (SO_4^{2-}) and phosphate (PO_3^{2-}). Squeira (1982) pointed out that sulfate and nitrate are not quantitative indicators of acid deposition unless the relative alkali deposition is negligible or corrected for neutralization. In principle, changes in pH can be brought about as well by changes in the concentrations of neutralizing substances as by changes in the concentrations of the strong acids. Substances which are recognized for their abilities to neutralize the atmospheric acidic load are fine wind-blow soil particles (Ca and Mg), K and NH_3 (Bubenick, 1984, Das *et al*., 2005). Neutralization of the acids by these base cations are validated by calculation of the neutralization factors (NF) by following equations (Possanzini *et al*., 1988).

$$NF = \frac{[X_i]}{[SO_4^{2-}] + [NO_3^-]} \tag{1.24}$$

where X_i is the chemical component of interest, with all the ions expressed in μeq/L

When the NF value of one specific component, it means that the component plays major roll in acid neutralization. Normally, NH_4^+ and Ca^{2+} are the dominant neutralization substances depend on the sampling site. On the other hand, neutralization by Mg^{2+} and K^+ is negligible i.e. Kulshrestha *et al*., 1996; Hu *et al*., 2003; Tehpanondh *et al*., 2005 and Das *et al*., 2005.

1.8.2 Marine and non-marine contribution

Normally, the ionic components in rainwater such as Cl^-, SO_4^{2-}, K^+, Ca^{2+} and Mg^{2+}can be come from earth crust, volcanoes, anthropogenic or even ocean (Das *et al*., 2005). Therefore, in order to estimate the marine and non-marine contribution to different ionic species in rainwater, enrichment factor (EF) and sea salt fraction (SSF) have been calculated.

The enrichment factor is a ratio used to discriminate aerosol sources (Ahmed *et al*., 1990, Singer *et al*., 1993, Akkoyunlu and Tayanc, 2003). This calculation is based on the element ratio found between ions collected in the atmosphere or in precipitation compared with a similar ratio for a reference material, provides important information on the sources of the elements of concern, enrichment factors for component *X* is calculated by using the following equation;

$$\mathrm{EF}(X) = \frac{(X/\mathrm{C})_{\textbf{precipitation}}}{(X/\mathrm{C})_{\textbf{reference material}}} \qquad (1.25)$$

where, *X* is the concentration of the ion of interest and 'C' is the concentrations of the reference ion (Bayraktar and Turalioglu, 2005, Das *et al*., 2005). In soil material, Ca^{2+} is chosen as the reference ion (e.g. Bayraktar and Turalioglu, 2005), while Na^+ is chosen in seawater contribution (Kulshrestha *et al*., 1996). However, the above reference ions may not be strictly for a typical site.

In the event that the EF value is much smaller than 1 or much greater than 1, it will be considered as concentrated or diluted relative to the reference source (Okay *et al*., 2002).

The sea-salt fractions (SSF) or non sea-salt fractions (NSSF) of any component can be calculated using the following equation (Das *et al*., 2005, Akkoyunlu and Tayanc, 2003).

$$\mathrm{SSF}(X) = [\mathrm{Na}^{+}_{\mathbf{rain}}][X/\mathrm{Na}^{+}]_{\mathbf{seawater}} \qquad (1.26)$$

$$\mathrm{NSSF}(X) = [X_{\mathbf{rain}}] - [\mathrm{Na}^{+}_{\mathbf{rain}}][X/\mathrm{Na}^{+}]_{\mathbf{seawater}} \qquad (1.27)$$

where $X_{\mathbf{rain}}$ is the concentration of component X in rainwater.

The recommended sea water ratio of $[X/\mathrm{Na}^{+}]_{\mathbf{seawater}}$ is shown in table 1.9 (Akkoyunlu and Tayanc, 2003).

Table 1.8 The recommended sea water ratio (ratio are mol/mol)

	Cl^-	SO_4^{2-}	Mg^{2+}	K^+	Ca^{2+}
Sea water ratio[a]	1.166	0.0603	0.1137	0.0218	0.0219

[a] With respect to Na^+

If sea salt fraction value of X is higher than sea water, it can be deduced that the component X is not from marine origin.

1.8.3 Identification sources of acid deposition

During the last decade, a number of studies on statistic which used to identify source of acid deposition in rainwater have been carried out in the world (e.g. Xu *et al*., 2007, Sakihama *et al*., 2007, Thepanondh *et al*., 2005, Akkoyunlu and Tayanc, 2003, Bravo *et al*., 2000, Bayraktar and Turalioglu, 2005, Saxena *et al*., 1996). These statistics are Pearson correlation (*r*) and principle component analysis (PCA). Pearson correlation is the statistic value to identify possible relationships between the various ionic species in wet deposition. Strong correlation value between two ionic species can suggest that these ions are potentially important compounds in wet precipitation and can be assessed that this ions are come from same origin.

Principle Component Analysis (PCA) or factor analysis is the statistical test for determination the factors underlying the inter-correlations between the measured species. Initial factors are extracted from a matrix of correlations derived from standardized variables. Each variable were also evaluated for its KMO value (Kaiser-Meyer-Olkin) and was included in the matrix only if it had a KMO value greater than 0.6. Finally, factors with eigenvalues greater than one were considered for varimax rotation to obtain the final factor matrix (Saxena *et al*., 1996). Factor analysis assumes that the inter-correlations among the original variables are generated by some smaller number of unobserved factors (Kessler *et al*., 1992). Comray (1973) explained that data loading more than 0.5 are deemed to be statistically significant. If ether of factor has data of (Na^+ and Cl^-), (NO_3^- and SO_4^{2-}), (Mg^{2+}, Ca^{2+} and SO_4^{2-}), H^+, NH_4^+, K^+ loading more than 0.5, it can be suggest that source of wet deposition are from marine origin, combustion process, soil resuspension, power plant, biogenic, biomass burning, photochemical reaction (Sakihama *et al*., 2007, Thepanondh *et al*., 2005, Hu *et al*., 2003, Fornado and Gutz, 2001, Saxena *et al*., 1996).

1.9 Research Objectives

1. To monitor acid deposition in Chiang Mai
2. To analyse acid deposition samples both in forms of wet and dry deposition
3. To prepare a database for controlling and reducing the effects of acid deposition on the environment and human health