CHAPTER 1

INTRODUCTION

1.1 Introduction

In the past few years, the problems of acid deposition (acid rain) and unexplained forest decline in Europe and North America have attracted considerable public and scientific interested. Discussion of these issues is often characterized by alarming claims and scenarios, as well as debate over the extent to which a serious problem actually exists.

Deteriorating air quality in Asia has wide-ranging consequences. Many urban centers in Northeast Asia have air pollution levels exceeding WHO ambient standards (Mage *et al.*, 1996 and Florig, 1995). Acidic precipitation is being reported throughout the region (Khemani *et al.,* 1989, Mohammed and Kamsah, 1993, Wang and Wang, 1995), with many areas already receiving levels, which exceed the acidic carry capacity of their soils (Hettelingh *et al.,* 1995). According to a recent study conducted by the Chinese Research Academy of Environmental Sciences, 40% of China is affected by acid rain, causing US$ 1.6 billion worth of damage to crops, forests and property annually (Walsh, 1995). The transport and fate of sulfur in Asia is an area of increasing environmental interest and concern (Carmichael and Arndt, 1995, Robertson *et al.*, 1995, Arndt *et al.*, 1996, Sato *et al.*, 1996, and Sharma *et al.*, 1995) as countries receive growing amounts of sulfur from neighboring and even distant countries (Ichikawa and Fujita, 1995, and Arndt *et al.,* 1996b).

1.2 Acid deposition

Acid deposition is widely recognized as one of the most serious atmospheric environmental issues. It is important to realize that the relationships between the emissions of pollutants and the resultant acid deposition are difficult to determine because of the number and nature of the processes that occur. As their economies expand, many countries, face increasing risks of acidic environmental pollution.

Acid deposition refers to the deposition of acidifying compounds from the atmosphere into our environment. The acidifying compounds are formed within the atmosphere through chemical reactions involving sulfur and nitrogen emissions. Wet deposition is more commonly known as acid rain and occurs when acidic droplets fall to earth. Dry deposition occurs when acidic substances react directly with soil, plants and water.

Sulfur and nitrogen cause acidification of precipitation (rainwater is classified as acidic if its pH is less than 5.6), which in turn can result in adverse environmental impacts. However, pH by itself is only part of the problem. It is not the pH of the rainwater that causes environmental problems, but rather the response of plants and soils to the chemical constituents of the rainwater. Of most concern is the presence of strong acids such as sulfuric and nitric acids.

1.3 pH of rainwater

pH is one of the important indices of rain. The measurement of rainwater acidity is a measure of its hydrogen ion concentration. It is normally expressed in terms of a pH value. On a pH scale of 0 to 14, a value of less than 7.0 is acidic, pH 7.0 is neutral and a pH value greater than 7.0 is alkaline. However, the relationship between pH value and acid concentration, in other words, the concentration of hydrogen ion, is rather complex. The lower the pH value is, the higher the hydrogen ion concentrations are. Hydrogen ion concentrations increase more rapidly at lower pH values. pH values depend on the balance of acids and bases. Even if rain contains a high concentration of nitric and sulfuric acids and has a low pH, the pH value will become higher with more bases like ammonium. Therefore, even rain with high pH may cause problems and attention must be paid to the concentrations of sulfuric and nitric acids as well.

1.4 Acid rain

Robert Angus Smith was the first who used the term of acid rain in 1872. He found that air pollution from burning of fossil fuels is the major cause. The main chemicals that create acid rain are SO_2 and NOx. Both NOx and SOx have been implicated in the occurrence of acid rain around the world. Normal precipitation has a pH of about 5.6, based on theoretical calculations that postulate equilibrium with CO_2 in air and with no other chemical substances affecting pH. However, even under pristine conditions, rainwater is often more acidic. Typical pH values of acid precipitation caused by human emission may be 3.5-5.0. Ammonia emissions will neutralize the precipitation, but may cause soil acidification through nitrification.

Because rain travels over long distances in clouds, acid rain is a global problem. In Britain, the prevailing winds come from the Atlantic, so they are unpolluted. This means that 87 percent of the SO_2 in the air in Britain is produced by industries etc. and only about 1 percent is natural. In Thailand a large portion of the Bangkok regional area has precipitation of pH values between 4.7-5.8. Every country with a power station or a significant number of road vehicles helps to generate the gases which cause acid rain. Therefore, it is a global problem, which needs a global solution.

1.5 Causes and mechanisms

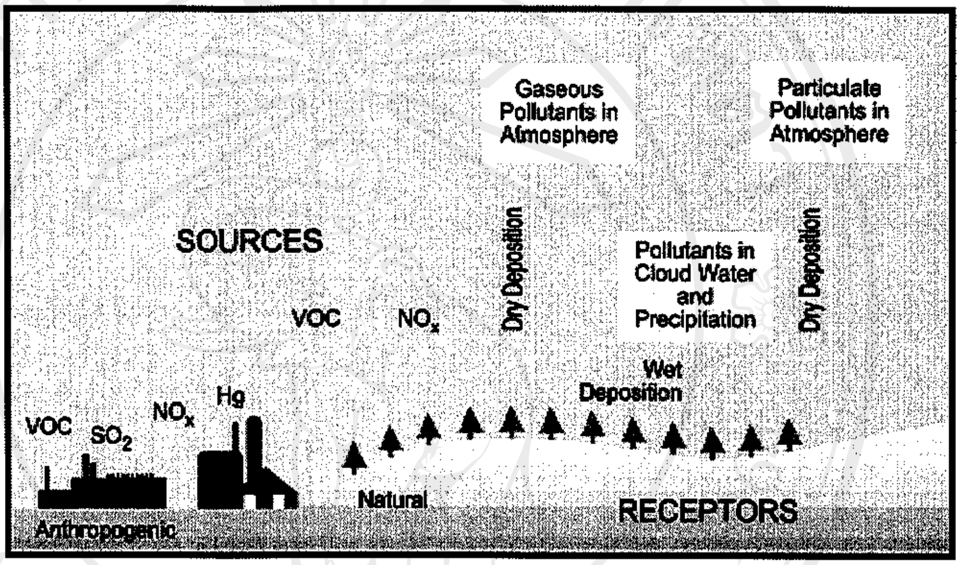
1.5.1 Acid deposition

Air pollution from the burning of fossil fuels is the major cause of acid deposition. The main chemicals that create acid deposition are SO_2 and NOx. Acid rain usually forms high in clouds where SO_2 and NOx react with water, oxygen and oxidants. This mixture forms a mild solution of sulfuric acid and nitric acid. Sunlight increases the rate of most of these reactions. Rainwater, snow, fog and other forms of precipitation containing these acids fall to earth as acid rain (Figure 1.1).

Acidic deposition is a global environmental issue originating from emission of pollutants in to the atmosphere. Acidic deposition affects ecosystems directly and indirectly. In Europe and North America, acidic deposition has seriously affected watercourses and in some areas forests are threatened (Babich *et al.,* 1980, Paces, 1985, Irwin and Williams, 1988, Cerny and Paces, 1995).

1.5.2 Acid rain

Acid rain refers to all types of precipitation such as rain, snow, sleet, hail and fog. "Acidic" means a pH lower than 5.6. Acid rain is simply rain, which is acidic. Natural rain has a pH level of 7, which is neutral. The acidity of rain is determined by the pH of pure water in reaction with atmospheric concentrations of carbon dioxide, resulting in carbonic acid. These particles partly dissociate to produce hydrogen ions and bicarbonate ions. Bicarbonate is formed by one ion hydrogen atom, one carbon atom and three oxygen atoms and is very effective in natural waters at neutralizing hydrogen ions and reducing acidity. This dissociation-results in the natural pure rain, which is moderately acidic at a pH of 5.7. Inorganic ions in rainwater such as cations and anions were shown in Table 1.1.



Source: United States of Environmental Protection Agency, 2002

Figure 1.1 Mechanism of acid deposition

Table 1.1 Important inorganic ions species in rainwater

Cations	Anions
H^+	Cl^-
NH_4^+	NO_3^-
Na^+	SO_3^{2-}
K^+	SO_4^{2-}
Ca^{2+}	PO_4^{2-}
Mg^{2+}	CO_3^{2-}

Source: U/S National Research Council, 1983

Rain with a pH of less than 5.6 is considered acid rain, meaning that it has reacted with acidic atmospheric gases other than carbon dioxide, such as SO_2 and NOx. SO_2 produced by electric utilities, industrial, commercial and residential heating, smelters, diesel engines and marine and rail transport, creates sulfuric acid in rain. NOx produced from transportation (cars, trucks, planes, etc.) and electric utilities will also react with rain, producing nitric acid. (Babich *et al.*, 1980). About 70% of acid rain comes from SO_2, which dissolves in water to form sulfuric acid. The rest comes from various oxides of nitrogen (mainly NO_2 and NO_3, collectively called NOx). These gases are produced almost entirely from burning fossil fuels, mainly in power plants and from road transport. Natural sources that emit sulfur dioxide include volcanoes, sea spray, plankton and rotting vegetation. Despite these natural occurrences, the burning of fossil fuels (such as coal and oil) can be largely blamed for the emissions (Babich *et al.*, 1980).

1.6 Impacts of acid rain

Economic losses from acid rain in the United States were estimated overall at about $13,000 million annually in the eastern part of the nation including $1,750 million yearly in forest damage, $8,300 million in crop damage in the Ohio river basin alone by about the year 2000 and $40 million in health costs in the State of Minnesota (Postel, 1984).

The effects of acid rain have been recorded in parts of the United States, Federal Republic of Germany, Czechoslovakia, the Netherlands, Switzerland, Australia, Yugoslavia and elsewhere. It is also becoming a significant problem in Japan and China and in Southeast Asia (Kuylenstierna *et al.*, 2001).

Acid rain harms the environment by contact with plants, soil and water for example, and by mobilizing trace metals. The effects of acid rain on plants, soil, and water in turn affect other living organisms that depend on them (Figure 1.2).

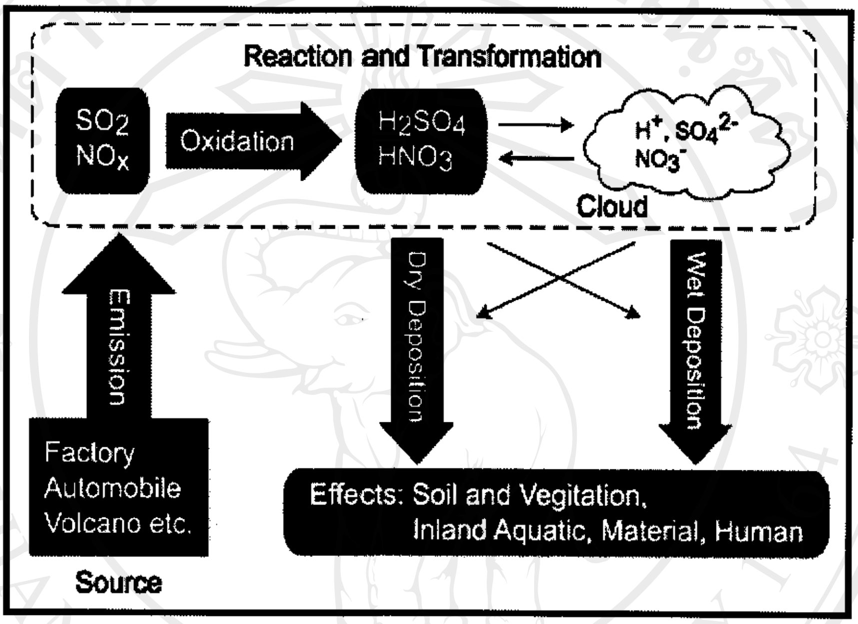


Figure 1.2 Impacts of acid rain

The forests of the Federal Republic of Germany and elsewhere in Western Europe, for example, are believed to be dying because of acid rain. Scientists believe that acid rain damages the protective waxy coating of leaves and allows acids to diffuse into them, which interrupts the evaporation of water and gas exchange of the the plant. This stops the plant's conversion of nutrients and water into a useful form for plant growth and affects crop yields (Postel, 1984).

Perhaps the most important effects of acid rain on forests result from nutrient leaching, accumulation of toxic metals and the release of toxic aluminum. Nutrient leaching occurs when acid rain adds hydrogen ions to the soil which interact chemically with existing minerals. This displaces calcium, magnesium and potassium from soil particles and deprives trees nutrition. Toxic metals such as lead, zinc, copper, chromium and aluminum are deposited in the forest from the atmosphere. Acid rain releases these metals and they stunt the growth of trees and other plants and also altered the growth of mosses, algae, nitrogen-fixing bacteria and fungi (Friedman *et al.*,1988).

1.7 Impacts of acidic rain on soil

Acid rain came destroy soil and water resources. Acid rain can cause minerals in the soil to dissolve quickly and it can reduce this source of minerals. It takes million of years to replenish the rocks that supply the parent material for soil. Many minerals are nutrients for both plants an animal (Brinkman and Pons, 1973). Soils have been affected by acidic deposition are poor in cations have developed on alluvial sediments, glacia till, sandstone and granite (Brinkman and Pons, 1973). Department of Agriculture and the Cooperative Promotion Department, Thailand determined the soil quality index that present nutrients concentrations in soil as shown in Table 1.2.

Soil acidification, which is usually related to reduced amounts of exchangeable base cations in the soil, has occurred in Europe, North America and likely also in China. Watmough and Dillon (2001) in a study in central Ontario estimated losses of calcium and magnesium over a 16-year period (1983 to 1998) representing 37 percent and 59 percent of their respective exchangeable pools measured in soils in 1983. Since a number of factors may cause soil acidification, e.g. vegetation changes, it is often difficult to determine the contribution from acid deposition.

Table 1.2 Nutrients concentrations in soil

Type of nutrients	Soil quality index		
	low	medium	high
Organic matter (%)	< 1.8	1.8-3.0	> 3.0
Phosphorus (ppm)	<10	10-30	>30
Potassium (ppm)	<40	40-100	>100

Source: Department of Agriculture and the Cooperative Promotion, 1998.

Soil acidification is an indirect cause of forest decline (Hauhs and Ulrich, 1988; Heij *et al.*, 1991; Matzner and Murach, 1995). For example, yellowing of spruce needles was attributed to magnesium deficiency in needles due to magnesium depletion in soil profiles.

Van Breemen (1983) also noted that at a lower pH, more H^+ can be immobilized because exchangeable Al^{3+} enters the soils solution. With large specific surface areas and the negative change associated with clay minerals, the soil solid phase can be important in immobilizing excess acidity. In soils with high organic matter and clay contents, the absorption of H^+ associated with the formation of non exchangeable acidity may substantially neutralize strong acid under neutral to slightly acidic soil conditions. Between 5 and 10 mEq of acid per 100 g of soils is immobilized by the exchange complex of typical acidic sulfate soils in Thailand when pH drops from 7.5 or 7 to about pH 5 (Van Breemen,1983).

Prasittikhet (1989), in his experiments with rice seedlings in acidic sulfate and nonacidic sulfate soils, found that pH strongly influenced the solubility of aluminum in acidic sulfate soils. Acidic deposition accelerates soil acidification and induces aluminum dissolution. Soil acidification is commonly defined as a decrease in acid neutralizing capacity (Van Breemen *et al.,* 1983).

Acid soil problems are likely to arise once the pH falls below 5.6 and become more common when pH falls below 5. Dieback of Japanese cedar was reported in a wide region covering the western and northwestern areas of the Kanto plain and the cause of this has been discussed in terms of acidification of the soils, as well as magnesium deficiency, exposure to atmospheric ozone, excess supply of nitrogen compounds, and water deficiencies (Sekiguichi, 1987).

Acidic rain has direct effects on ecosystems. Air contaminants have some long-term effects on plants indirectly by influencing ambient CO_2 concentration, light intensity, temperature, as well as precipitation. The responses of plants to pollution vary with plant species and genetic make up, pollutant dosage, types and combination of pollutants, plant response parameters, developmental stage of plants, environmental regimes, and interactions of pollutants with plant diseases and insects (Kozlowski and Constantinidou, 1986b).

1.8 Impacts of acidic rain on plants

High yields of crops require an abundant supply of 16 essential nutrient elements from the soil (Table 1.3). In addition to providing a place for crops to grow, soil is the source for most of the essential nutrients required by the crop.

Acid rain damage in Germany in the Black Forest includes the death of saplings and "crown droop," the death of limbs at the top of the conifers. It can also prevent seeds from germinating. Plants growing in high altitudes (especially cloud forests) are the first to show the effects of acid rain because they are often literally in the clouds, essentially bathed in acid mist (Babich *et al.,* 1980; Paces, 1985).

The damage of acidic substances in rain water on forests and agriculture is well recognized in Europe and North America. Japan has seriously affected watercourses and forest in some areas are threatened (Babich *et al.,* 1980; Paces, 1985, 1986; Irwin and Williams, 1988; Cerny and Paces, 1995).

Acid rain can enter plants either as wet deposition (precipitation) or dry deposition (gas and aerosols), and damage plants or crops by causing them to lose their leaves. It does not usually kill trees directly. Instead, it weakens trees by damaging their leaves, limiting the nutrients available to them, or exposing them to toxic substances slowly released from the soil. In most cases, damage is caused by the combined effects of acid rain and other environmental stresses (Babich *et al.,* 1980).

Table 1.3 Essential nutrient elements in soil

Nutrient	Symbol	Form available	Category
Carbon	C	CO_2, H_2O	Non-fertilizer elements supplied through air, water, and soil nutrients
Hydrogen	H	H_20	
Oxygen	O	CO_2	
Nitrogen	N	$N0_3^-$, NH_4^+	Macronutrients required by plants in large amounts
Phosphorus	P	PO_4^{2-}	
Potassium	K	K^+	
Calcium	Ca	Ca^{2+}	Secondary nutrients required by plants in moderate amounts
Magnesium	Mg	Mg^{2+}	
Sulfur	S	SO_4^{2-}	
Boron	B	HBO^{4-}	Micronutrients required by plants in small Amounts
Chlorine	Cl	Cl^-	
Copper	Cu	Cu^{2+}	
Iron	Fe	Fe^{2+}, Fe^{3+}	
Manganesse	Mn	Mn^{2+}	
Molybdenum	Mo	$Mo0_4^{2-}$	
Zinc	Zn	Zn^{2+}	

Source: Baker, College of Agriculture and Home Economics New Mexico State University, 2002

Hypotheses that relate to acidic deposition and the decline of plants, currently receiving substantial research attention include (1) excess nitrogen deposition interfering with winter hardening of buds and foliage; (2) ozone-acid mist causing nutrient leaching from foliage; (3) soil acidification and cation leaching, leading to nutrient deficiency; (4) aluminum toxicity caused by soil acidification; (5) heavy metal; (6) direct gaseous oxidant effects, including ozone and hydrogen peroxide and (7) adverse meteorological conditions (Pitelka and Raynal, 1989).

However, long-term exposure to low concentrations of pollutants causes chronic injury to plants without visible damage. Reductions of growth and yields have been reported elsewhere. It is estimated that ambient air pollution related to crop damage amounts to billion of dollars each year in United State of America (Babich et al., 1980).

Figure 1.3 showed that plants are subjected to a combination of stresses, both from natural causes and human activities. Natural stresses include, drought, high temperatures, pathogens and predation, whereas human activities include physical disturbance and air pollution. Emission from lignite power plants is mainly SO_2, with minor contributions of other pollutants. The combination of these factors can cause additive, synergistic or antagonistic effects on plants. Once the damage from the air pollution starts, it can be difficult to reverse it. Increasing our understanding of the effects of ambient air pollution on the vegetation is necessary to elucidate the detrimental effects of air pollution, which can finally lead to strategies and policies to manage for sustainable development (Babich *et al.,* 1980).

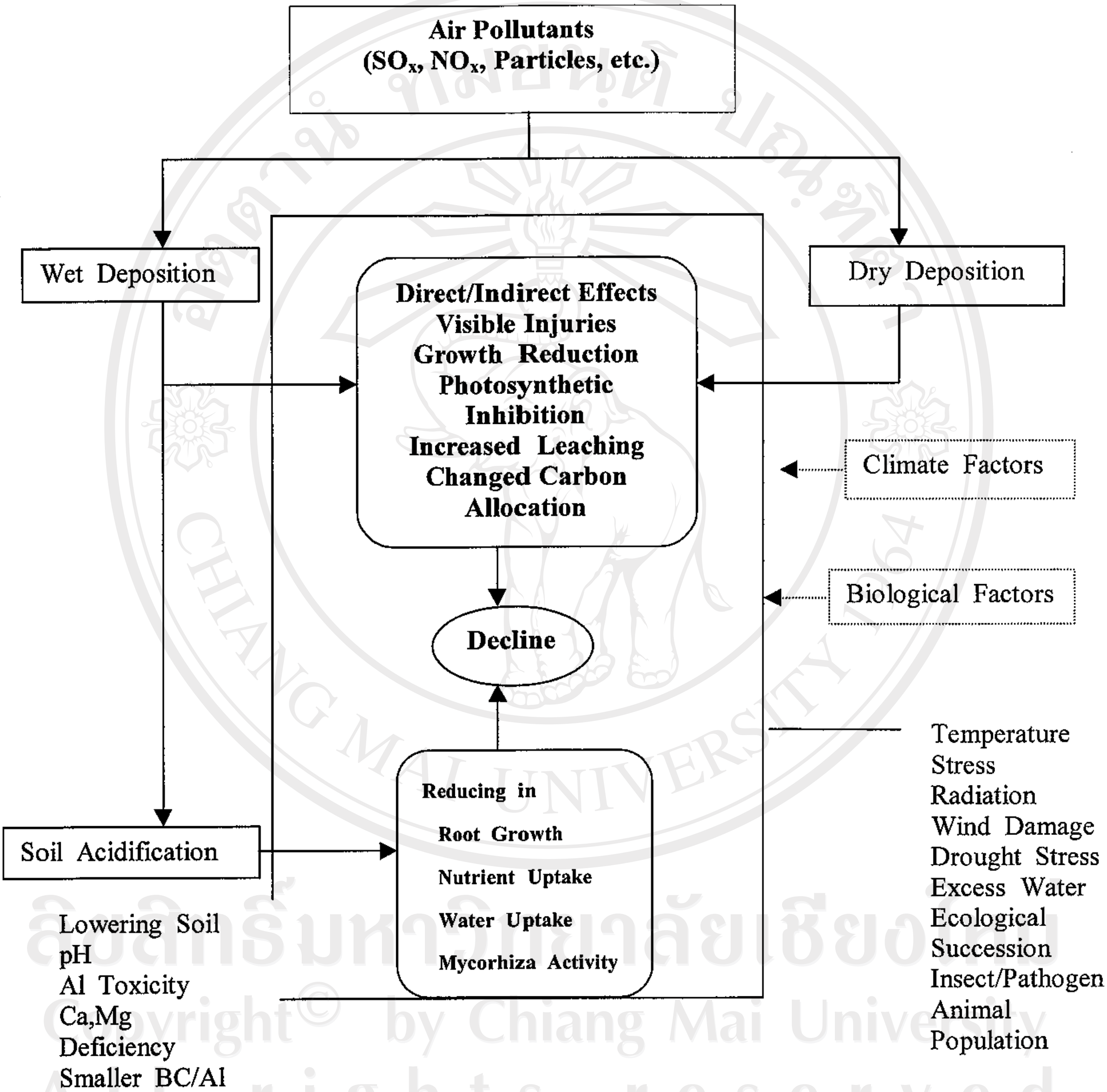


Figure 1.3 Pathway of plant decline impacted by acid deposition

At least three studies of the effects of acidic rain on seed germination have been conducted in North America. Eleven species subjected to simulated acidic rain

The deposition of acid and several heavy metals with ecotoxic significance contributes substantially to the burden of terrestrial and aquatic ecosystems and causes severe damage to the vegetation, e.g. forests, and aquatic organisms particularly in stagnant waters such as lakes and ponds. Besides these ecotoxic hazards, heavy metals also affect man, as they accumulate in vegetables and cereals. Of particular significance in terms of ecotoxicity is the fact that almost the whole amount of these wet deposited heavy metals are dissolved in rain and thus reach the ground in a state most favorable for uptake by the vegetation and natural waters (Nurnberg *et al.,* 1984).

1.8.1 Impacts on seed germination

Kuja, Jones and Enyedi (1986), conducted a study to determine the effects of simulated acidic rain conducted on seed germination, seedling establishment, and early stages of plant growth. Visible foliar injury was only observed at pHs between 3 and 2.6. Cultivar responses varied, indicating that, for yields or growth effects, plant response is not only species-dependent but also strongly cultivar dependent. In addition, Abouguendia, Baschak, and Godwin (1986), conducted similar controlled growth experiments with six Saskatchewan forest and crop species, showed that simulated acidic rain with pH 3.6 or higher had minimal effects on the crop and forest species studied.

Raynal *et al.*(1982), Dustin and Raynal (1988) reported that seed germination and early seedling growth of sugar maple are not adversely affected by acidic precipitation at current ambient levels.

At least three studies of the effects of acidic rain on seed germination have been conducted in North America. Eleven species subjected to simulated acidic rain pH values from 5.6 to 3.0, significant stimulation of germination was shown for five species at pH 3 (Lee and Weber, 1979). Inhibition of germination in *Pseudotsuga menziesii* was observed at simulated acidic rain of pH 2.0 (McColl and Johnson, 1983), whereas stimulation was observed in this species at pH 3.0 (Lee and Weber, 1979). Inhibition in additional species was observed between simulated acidic rain pH 2.5 and pH 4.0, whereas stimulation of germination was found in *Pinus strobus* at simulated acidic rain pH values between 2.0 and 3.0 (Raynal *et al.,* 1982). Studies by Raynal et al., (1982) indicated that, at least for some species, seed germination is less sensitive to acidic precipitation than is subsequent seedling establishment. Although seed germination was unaffected by the acidic treatment. Growth of *P. strobus* seedlings receiving simulated acid rain of 5.6, 4.0, 3.5, or 3.0 was little affected when planted in relatively N-rich soil. In relatively N-poor soil however growth was accelerated in the pH 3 treatment due to an N fertilization effect (Reich *et al.,* 1987).

1.8.2 Impacts on seedlings

Few studies have been conducted on the effects of acidic precipitation on seedling survival. Seedling of *Pseudotsuga menziesii* germinating at pH 2.0 died following erosion of cuticles, which permitted fungal attack (McColl and Johnson, 1983). *Pinus halepensis* Mill, subjected to simulated acidic rain of pH 3.0 showed 11% increased mortality compared to controls at pH 5.1 (Matziris and Nakos, 1977).

1.8.3 Impacts on tree growth

Studies of the effects of the simulated acidic rain on tree growth are produced conflicting results in the laboratory studies. Visible injury was often considered the primary indication of dose response or impact. The species which study shows that the upper pH limit for injury is about 3.0 for both conifers and deciduous species (RMCC, 1986). While atmospheric pollutants significantly affected reproductive processes at pHs below 5.6 (Cox, 1987). In Japan, Sekiguichi (1987) reported dieback of Japanese cedar in the western and northwestern areas of the Kanto plain.

1.8.4 Visible impacts on plants.

Simulated acidic rain at pH 3.0 in the greenhouse causes visible injuries to leaves, stems, and flowers. Plant response is dependent on the total dose of acidity, as well as intensity, frequency and quantity of the rain event, although foliar injury is not a reliable means of assessing actual effects on crop yields (Enyedi and Kuja, 1986).

Acidic rain with pH 5.0 causes moderate damage to plants by the end of the second day and pH 2.0 causes damage within a few minutes with most plants dieing by the end of the second day (Riediger and Smith, 1998). Injuries to soybeans are significantly higher than to other plants receiving acidic treatment pH 3.0 (Banwart *et al.*, 1990). Japanese conifers exposed to simulated acid rain at pH 2 develop visible foliar injuries, but at pH 3.0 or higher there are no visible symptoms (Kohno *et al.*, 1995).

Possible explanations of red spruce decline include climatic factors, disease, natural senescence, gaseous pollutants and acidic precipitation (Hornbeck *et al.*, 1986).

1.9 The status of acid deposition in Asia

Acid rain in Japan has been monitored at Ryouri since 1976. The pH levels were 5.2 in 1970's and below 4.7 at present. The acidity is predominately due to sulfate and nitrate, with sulfate contributing 3 times more acidity than nitrate (Hara ,1993 and Murano *et al.*, 1993).

In 1989, the Japan Environmental Agency (JEA) organized monitoring of acid deposition which continues till now. Data from 29 sites, throughout Japan, showed that annual pH values range from 4.3 to 5.3, with sulfate again being the major acid followed by nitrate. These values can be compared to those measured in Europe and North America where the values range from 4.4 to 6.5 and 4.2 to 5.6, respectively. The pH levels in Japan are similar to those measured in areas in Europe and North America where acid deposition problems have occurred.

China began surveys of acid deposition in 1982, under the auspices of the Chinese National Environmental Protection Agency. Wang and Wang (1995) reported that the pH values of rainwater in the western half of China ranged from 6.0 to 7.0. In southeastern regions, pH levels are strongly acidic, the annual mean values falling below 4.0. The northeast region of China has higher pH levels than in the south. The contour of pH levels equal to 5.6 extends to the west of Beijing and along the eastern edge of the Greater Khingan mountain range. The regions receiving acidic deposition in 1982 were restricted to the southeast regions well below Beijing. The area receiving acid deposition has increased by 600,000 - 700,000 km^2 since 1982 (Wang *et al.,* 1995).

1.10 The status of acid deposition in Thailand

In the past few years, air pollution has become a major environmental problem in Thailand, associated with consumption of fossil fuels. Major sources of SO_2 include natural gas processing, crude oil and coal-fired power plants. Major sources of NOx are auto exhaust and various industrial activities, including oil and gas production, oil refining, electricity generation and residential fuel combustion. These problems will become enormous in the future, with a projected increasing demand for fossil fuels for energy production. More importantly, natural vegetation in the tropics is rich in biodiversity.

Thailand has experienced the impact of acid rain since 1992, due to SO_2 emitted from the Mae Moh lignite-fired power plant in the north. The power plant burns high-sulfur lignite without SO_2 emission control. The Pollution Control Department (2000) reported the impacts on human health and vegetation in the area nearby the power plant (Figure 1.4).

Measurements on the acidity of rain have been made at different locations in Thailand over many years. The pH of rain in Chiang Mai in 1988 was in the range of 5.6-6.9, with a minimum pH of 4.8. Acidity was in a range of 2.5-5.0 mg/l. Sulfate content in rain water was in the range of 1.0-3.0 mg/l. (Im-Erbtham and Wongnopparat, 1988). Annual average pH's of rainwater from 1997 to 1999 were 5.6, 5.18 and 5.73 in Bangkok, 6.2, 5.13 and 5.08 in Rayong, 6., 5.84 and 5.81 in Kanchanaburi, and 5.64, 5.68 and 6.28 in Lampang (The Pollution Control Department, 2000). In addition, the pH of rainwater at Prathumthanee Province between August to September 1997 ranged between 4.64 and 6.8, and some areas had high concentrations of SO_4^{2-} and Ca^{2+} (The Environmental Research and Training Center, 2000).

Figure 1.4 Impact of acid deposition on human health and vegetation in Mae Moh area

1.11 Research objectives

The impact of air pollution on vegetation in Thailand has not been studied in detail. Moreover, the impact of acid rain on economic plants such as rice, tobacco, tomato, pole bean and cucumber in Thailand has not yet been quantified, especially threshold doses, at which damage becomes significant.

Therefore, the major concerns of this study were rainwater, soil and plants. The objectives of this thesis were;

1) To determine the sensitivity of various crop plants to acid rain.
2) To investigate the effects of acid rain on nutrient uptake and plant morphology.
3) To analyze the acidic substances that accumulates in rainwater, soils and plants.