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Chemistry and mineralogy of acid sulfate soils and potential utilization of green manures as acid soil amendments

Poolpipatana, Sunthorn, Ph.D.

University of Hawai‘i, 1994
CHEMISTRY AND MINERALOGY OF ACID SULFATE SOILS AND POTENTIAL
UTILIZATION OF GREEN MANURES AS
ACID SOIL AMENDMENTS

A DISSERTATION SUBMITTED TO THE GRADUATE DIVISION OF THE
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DOCTOR OF PHILOSOPHY

IN

AGRONOMY AND SOIL SCIENCE

MAY 1994

By

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ACKNOWLEDGEMENTS

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ABSTRACT

Potential and actual acid sulfate soils in the Bangkok Plain are strongly acidic, high in solution Al, Fe, Mn and low in Ca in the unamended state. For successful intensive crop production, lime and green manure applications are necessary. The use of locally available green manures, as "a self-liming material" is a promising strategy for alleviating Al toxicity and raising the concentration of basic cations in the soil solution.

The growth and acidity tolerance of four tropical legumes (Pigeon pea: *Cajanus cajan*, *Sesbania aculeata*, *S. rostrata* and *S. speciosa*) were studied in a greenhouse experiment for potential green manure sources. Two acid sulfate soils (Typic Sulfauquents, Bang Pakong (Bg) series; and Sulfic Tropaquepts, Rangsit (Ra) series) were adjusted to four pH levels: 3.8 or 4.0 (original soil pH), 4.5, 5.5 and 6.5 (amended with lime). Based on green manuring criteria of high biomass production and high N content, *C. cajan* and *S. aculeata* were better suited to the acid sulfate soils than *S. rostrata* and *S. speciosa*. The legumes responded differently to stresses imposed by Al toxicity. *C. cajan* tolerated nearly three times the level of Al as the *Sesbania* species: Critical Al concentrations in shoots (for 10% dry matter reduction) were 80 mg kg\(^{-1}\) for the former and 30 mg kg\(^{-1}\) for the latter.

A greenhouse experiment was conducted to quantitatively compare the effects of two green manures (0, 20, 40, 80 Mg ha\(^{-1}\)
ground tops of *S. aculeata* and *C. cajan*) and lime (0, 4, 8 Mg CaCO₃ ha⁻¹) on Al detoxification for upland rice grown for 60 days in two acid sulfate soils. Green manure applications effectively detoxified Al. *C. cajan* was better than *S. aculeata* in reducing Al⁺³ activities in soil solution. Green manure and CaCO₃ amendments were compared by estimating amounts of the materials required to decrease Al⁺³ activity until relative root length of the rice plants were ≥ 90%. The application rates of CaCO₃, *C. cajan* and *S. aculeata* required to meet this criterion were 5.3, 44.4, 57.5 Mg ha⁻¹, respectively.

An incubation study for 90 days was conducted to determine changes in the solid phase, the solution phase, and mineralogical properties of representative acid sulfate soils following lime (CaCO₃ 6 Mg ha⁻¹) and green manure (sesbania 40 Mg ha⁻¹) applications. In the unamended soils, strong acidification occurred, resulting in pH decreases to ≤ 2.8. By contrast, liming and green manuring increased soil pH, EC, total exchangeable bases, and reduced Al saturation percentage. X-ray diffraction analysis showed no detectable change in soil minerals by either amendment in spite of strong acidification occurring in the control. Detailed mineralogical study of handpicked yellow particles from soils at 90 days after incubation showed the presence of jarosite. Soil solution analysis suggested that jarosite might be formed by precipitation of K⁺, Fe⁺³ and SO₄⁻². Based on the ion activity
products and stability diagram, lime and sesbania applications resulted in the formation of Al-hydroxy sulfate minerals. The $^{40}$Ar activities were pH dependent and apparently controlled by the solubility of an alunite-like mineral, $\text{KAl}_3(\text{OH})_6(\text{SO}_4)_2$, having a $\text{pK}_{sp}$ of 81.4.
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CHAPTER 1
Introduction

Of the total 12.5 million hectares of reported potential and actual acid sulfate soils in the world (Dent, 1992), 1.5 million hectares occur in Thailand. Among these, 0.9 million hectares are located in the Bangkok Plain. The remainder are found in various parts of the eastern coast, and on the peninsular which makes up the southern region (Parkpian et al., 1991).

Generally, acid sulfate soils have very low pH, and originate from saline and brackish marine sediments. These soils are formed in coastal regions where large quantities of pyrite (FeS₂) have accumulated in intertidal sediments. Pyrite accumulation is a result of anaerobic conditions, which cause sulfate (SO₄²⁻) from sea water to be reduced to sulfide (S²⁻). The alkalinity formed during sulfate reduction is leached from the sediments by tidal action, leading to a potential acidity. If these soils are aerated, either by natural or artificial drainage, pyrite will be oxidized to sulfuric acid and the soils are acidified. As a result, the pH drops below 4. In this situation, hydrogen ions, aluminum, iron, manganese, and organic acids can accumulate to levels toxic to plants. Therefore, plants are unlikely to grow well unless the soils are ameliorated. An extremely low pH (3.0) at the surface layer characterizes young acid sulfate soils. This type of soils (Sulfaquents) has been found in large areas in some
countries such as Indonesia (Alkasuma et al., 1990), Vietnam (Xuan, 1993), and Malaysia (Ting et al., 1993).

As these soils age, characteristic minerals are formed. The important minerals found in developed acid sulfate soils are jarosite, alunite, goethite, hematite, ferric hydroxide, and gypsum. Because these soils contain neutralizable base and the stepwise potentially reserved acidic substances (e.g., jarosite), soil pH's appear to be maintained at 4.0. The more mature these soils are, the deeper the jarositic and the pyritic horizons are, resulting in surface soils with higher pH. At this stage, however, the soil conditions are very adverse to plant growth, and yields are low.

The Bangkok Plain is the main rice growing area of Thailand. This plain is essentially a river valley widening to coastal plain and crossed by various bifurcations of the rivers and tidal channels. During the rice growing season, the plain is inundated by river floods and rain water. Under the prevailing water conditions one rice crop per year is the rule, and yield production ranges between 0.5 and 2.5 tons ha⁻¹. Low productivity (0.5 - 1.5 tons ha⁻¹) is associated with a large complex of nearly 0.6 million hectares of acid sulfate soils in the central part of the Bangkok Plain (Attanandana, 1990).

Acid sulfate soils have predominantly developed soil profiles with characteristics of Sulfic Tropaquepts. They developed in pyritic (1 - 2.5 % S) non-calcareous gray clays,
deposited in a brackish tidal environment 3 - 7 thousand years ago. More recent fluviatile and marine deposits of adjacent upstream and downstream parts of the Plain gave rise to soils without acid sulfate conditions, of higher productive potential, and characteristics of predominantly Typic Tropaquepts.

The processes involved in soil genesis of acid sulfate soils of the Bangkok Plain and their behavior on drying and flooding have been studied by van Breemen (1976) and their fertility amelioration by Ponnamperuma et al. (1973) and Attanandana (1982). Fertility studies have shown that acid sulfate soils are generally well developed physically, but their high acidity retards microbiological activity. Possible causes of poor plant performance have been identified as Al and Fe toxicities and deficiencies of N, P, and Ca.

Methods to control acidification during reclamation and to prevent or improve collateral adverse soil conditions, should be developed to suit specific agro-ecological situations. In the Bangkok Plain, this development has been initiated since 1970 (Komes, 1973; Jugsujinda et al., 1978; Charoenchamratcheep et al., 1982, Satawathananont, 1986; Moore et al., 1990) and has focused on improving acid sulfate soils for rice cultivation. The most commonly used management strategy for these soils is liming. Since a large quantity of marl has been found at a shallow depth nearby, liming has been widely recommended. Because of differences among acid sulfate soils
and the variation in land use, both positive results and negative results with lime have been reported.

Leaching and submergence are also promising management practices for ameliorating acid sulfate soils. Leaching is usually manipulated after the soil has been exposed to oxidation and after subsequent flooding in order to dissolve toxic substances. Natural leaching by rainfall is preferred to artificial leaching because of scarcity of water resource and expenses in the dry season.

Submergence induces reduction processes caused by an insufficient supply of oxygen. Reduction causes numerous changes in the chemical, physicochemical, and microbiological properties of a soil. For instance, reduction decreases redox potential (Eh) and reduces sulfate, and increases pH, available iron, manganese, phosphorus, sulfide and organic acids. In contrast to submergence, drainage brings about oxidation and the reverse processes take place.

This dissertation aims mainly at developing alternative practices that prevent or alleviate the toxicity of acid sulfate soils used for growing rices, with emphasis on: (i) selection of Al tolerant plants to be used as green manures, (ii) incorporation of green manures into the soil so that soil acidity and Al phytotoxicity can be reduced, and (iii) identification of possible chemical and mineralogical changes of aluminum, iron and sulfate in acid sulfate soils as affected by green manure applications.
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CHAPTER 2

Problem statement, justification, and objectives

Along with soil solution chemistry, mineralogy plays an important role in acid sulfate soils. Both phases have marked effects on solubility, stability, and activities of many soil components, particularly toxic elements, such as Al$^{3+}$, Fe$^{2+}$ and Mn$^{2+}$. Therefore, effective management of acid sulfate soils would not be possible unless the chemical and mineralogical properties of such soils are better understood and modified. Unfortunately, most research papers presented at the International Symposium on Acid Sulfate Soils, which was first held in Wageningen, the Netherlands (Dost, 1973), then in Bangkok, Thailand (Dost and van Breemen, 1982), in Dakar, Senegal (Dost, 1988), and recently in Ho Chi Minh City, Vietnam (Dent and Mensvoort, 1993), dealt mainly with identification, mapping, pH and metal ion chemistry of acid sulfate soils. No detailed studies have been presented on the significant relationship between the chemical and mineralogical properties. The participants in these symposia did recognize, however, that one of the major limitations in the utilization and management of acid sulfate soils is a lack of understanding of chemical and mineralogical processes that control the release/sorption of the soil chemical constituents.
1. Selection and adaptability of green manures to Al tolerance in acid sulfate soils

In Thailand, a number of green manure legumes, e.g. *Sesbania, Sunn hemp, Vigna and Cajanus*, possess many ecotypes potentially tolerant to Al. They should be evaluated for their amendment value to acid sulfate soils. Liming such soils is not feasible in many cases, and subsoil liming is impractical. Therefore, the use of Al-tolerant green manure genotypes as soil amendments appears to be a reasonable approach. Fitting plants to soil conditions is sometimes more desirable and economical than adjusting soil conditions to plants.

2. Effects of green manure amendment on Al phytotoxicity in acid sulfate soils

Aluminum phytotoxicity is an important constraint to agricultural production. Managing Al toxicity requires the ability to predict or measure its severity then to control it. Two approaches will be adopted in this research towards reclamation of acid sulfate soils: to seek Al-tolerant ecotypes of green manures; and to ameliorate Al toxicity permitting growth of many important crops.

Amelioration requires that Al toxicity be sufficiently reduced to permit establishment and sustained growth of suitable crops by the incorporation of green manure which have passed the selection process or have shown a great ability to survive in very acid conditions. The reclamation process
consists of successful growing of Al-tolerant green manure plants followed by their incorporation to improve physicochemical properties of acid sulfate soils, and to increase crop yields.

3. Roles of aluminum, iron and sulfate in acid sulfate soils

Moore et al. (1990) indicated that the most important constraints on acid sulfate soils were related to the combined effects of low pH and Al toxicity, and Fe stress (high Fe and low base status). Strategies used in ameliorating acid sulfate soils include liming, leaching and organic amendments. Attanandana (1982) reported that both liming and leaching hastened a drop in the redox potential of submerged acid sulfate soils in Thailand. The addition of fresh organic matter has been found to accelerate soil reduction and shorten the period of high Fe$^{2+}$ concentrations (IRRI, 1976).

Reduction of Fe compounds is the most important process that causes pH increases following submergence of acid sulfate soils. Since these soils contain considerable amounts of S, the reduction of SO$_4^{2-}$ can also significantly increase soil pH at low redox potential (van Breemen, 1975). Earlier work has showed that reduced S species accumulate under anaerobic conditions, whereas SO$_4^{2-}$ concentrations increase under oxidized conditions (Charoenchamratcheep et al. 1987).

Several researchers have found that the pH's of most acid sulfate soils increase slowly as compared to normal soils and
the pH rarely exceeds 6.0, even after six months of submergence (van Breemen and Pons, 1978). The slow increase in pH has been attributed to adverse conditions for microbial reduction, low contents of metabolizable organic matter, and low contents of easily reducible ferric oxide (van Breemen, 1976). The high buffer capacity due to dissolved and exchangeable Al, adsorbed $\text{SO}_4^{2-}$ and basic sulfate mineral components would also require large amounts of Fe reduction to produce a significant increase in pH (van Breemen and Moormann, 1978).

Moore and Patrick (1991) found that oxidation of acid sulfate soils results in dramatic changes in metal solubility. In such dynamic systems, maximum dissolved $\text{Al}^{3+}$ activities appear to depend directly on pH and the activity of dissolved sulfate, presumably as a result of near equilibrium with $\text{Al(OH)}_2\text{SO}_4$, according to $p\text{Al(OH)}_2\text{SO}_4 = 17.2$. Because $p\text{SO}_4$ varies little and is close to 2.3 in most actual and potential acid sulfate soils, the relation $p\text{Al} = 0.9 + \text{pH}$ is sufficiently accurate for most practical purposes.

4. Objectives

This study focused on the chemistry of Al, Al containing minerals, and the relationship of Al with plant growth in acid sulfate soils. The goal is to properly manage acid sulfate soils for increased crop yields.

The specific objectives of this study are to:
1. Investigate the potential and adaptability of common green manure plants to acid sulfate soils;

2. Evaluate the effect of selected green manures on Al toxicity, growth and mineral nutrition of rice, and identify possible mechanisms responsible for Al detoxification;

3. Assess chemical and mineralogical changes in some acid sulfate soils amended with green manures.
References


CHAPTER 3

Genesis and chemistry of acid sulfate soils in the Bangkok Plain, Thailand; and potential problems for rice production

3.1 Occurrence of acid sulfate soils

Acid sulfate soils occur in all climatic zones with the majority of them being located in relatively recent coastal marine sediments. The sulfidic materials which produce acid sulfates on oxidation are not limited to coastal regions. They are often associated with inland pyritic material such as lignite. When such materials are brought to the surface through mining or other activities, sulfuric acid will be produced. Unfortunately, no detailed report on the upland acid sulfate soil acreage in the world is available. However, the upland acid sulfate soils have reportedly been found in Germany (Buurman et al., 1973), the Netherlands (Poleman, 1973; van Wallenburg, 1973), British Columbia and Alberta of Canada (Pawluk and Dudas, 1978), North Carolina and many other states in the United States (Carson et al., 1982), and Australia (Fitzpatrick et al., 1993).

From the FAO Soil Map of the World, Revised Legend (1991), it is estimated that there is a total area of 12.6 million hectares of lowland acid sulfate soils. Among these 6.7, 3.7, 2.1, and 0.1 million hectares occur in Asia and the Far East, Africa, Latin America, and North America, respectively. Dent (1992) also estimated that in recent coastal plains and tidal
swamps worldwide, there are some 12 - 14 million ha, mostly in the tropics, where the topsoil is severely acid, or will become so if drained. In addition, there may be twice this area of potentially acid material overlain by shallow peat or alluvium. Estimates of the extent and distribution of acid sulfate soils, however suffer more than most from scant field survey, unreliable laboratory data, and variable definition. In the Bangkok Plain, for example, van der Kevie and Yenmanas (1972) estimated an area of 760,000 ha of acid sulfate soils; but Osborne (1985), defining extreme acidity as base saturation < 50% and extractable aluminum > 5 cmol_c kg^-1, estimated the area of extremely acid soils as only 226,400 ha.

Some acid sulfate soils have developed naturally as a result of changes in hydrology or relative sea level, for example, those of the Bangkok Plain. In Senegal, a falling water table as a result of extended drought since 1971 has caused new acid sulfate soils on the low estuarine terraces and intertidal flats (Sadio and van Mensvoort, 1993). But extensive areas of acid sulfate soils have been developed as a result of deliberate land drainage.

On a global scale, acid sulfate soils are not extensive. They often occur in regions of critical population pressure, notably in the Southeast Asia and West Africa where other land for subsistence food production is not readily available. Distribution and classification of acid sulfate soils in the Southeast and East Asia are depicted in Table 3.1.
<table>
<thead>
<tr>
<th>Country</th>
<th>Area (10^3 ha)</th>
<th>Reliability</th>
<th>Soil Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bangladesh</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chittagong</td>
<td>200</td>
<td>-</td>
<td>Sulfatequents, Sulfaquepts</td>
</tr>
<tr>
<td>Khulna Sunderbens</td>
<td>500</td>
<td>-</td>
<td>Sulfatequents</td>
</tr>
<tr>
<td>Burma</td>
<td>180</td>
<td>-</td>
<td>Sulfatequents</td>
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<tr>
<td>China</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coastal areas (South of Rukien)</td>
<td>67</td>
<td>+</td>
<td>Sulfatequents, Sulfic Haplaquepts</td>
</tr>
<tr>
<td>India</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kerala</td>
<td>110</td>
<td>+</td>
<td>highly organic Sulfaquepts, partly 26,000 ha affected by salinity</td>
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<td>280</td>
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<tr>
<td>Indonesia</td>
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<td></td>
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<tr>
<td>Kalimantan and Sumatra</td>
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<td>-</td>
<td>mainly organic Sulfaquepts, partially Sulfatequents and Sulfihemists</td>
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<td>200</td>
<td>+</td>
<td>mainly Sulfatequents</td>
</tr>
<tr>
<td>Japan</td>
<td>4</td>
<td>++</td>
<td>Sulfatequents, Sulfic Haplaquepts</td>
</tr>
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<td></td>
<td>17</td>
<td>++</td>
<td>potentially acid shallow sea bottom</td>
</tr>
<tr>
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<tr>
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<td>highly organic Sulfaquepts and Sulfatequents</td>
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<td>3</td>
<td>+</td>
<td>Sulfic Haplaquepts, Sulfatequents</td>
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<td>Thailand</td>
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<tr>
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<td>++</td>
<td>Sulfic Tropaquepts (550,000 ha), Sulfatequents (±10,000 ha), Sulfatequents, Sulfatequents</td>
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<td>+</td>
<td>Sulfatequents, partly high organic matter</td>
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<td>Vietnam</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Me Kong Delta</td>
<td>1000</td>
<td>-</td>
<td>mainly Sulfatequents, smaller areas of Sulfic Tropaquepts and highly organic Sulfatequents</td>
</tr>
</tbody>
</table>

*Reliability: - (poor); + (fair); ++ (good);*  
*Gross estimates:*
3.2 Definition of acid sulfate soils

The definition given to "Acid Sulfate Soils" by Pons (1973) refers to all materials and soils in which, as a result of soil formation processes, sulfuric acid either will be produced, is being produced, or has been produced in amounts that have a lasting effect on main soil characteristics. Traditionally, the expression of "acid sulfate soils" is often used in a narrow sense for soils with "cat clay". The cat clay phenomenon is a combination of conspicuous straw-yellow jarositic mottles and a very low pH.

Brinkman and Pons (1973) categorized acid sulfate soils into three groups and defined soils in each group as follows.

1) A potential acid sulfate soil or material is a soil or reduced parent material which is expected by the person identifying it to become an acid sulfate soil or material upon drainage and oxidation under certain defined field conditions.

2) An actual acid sulfate soil is a soil with one or more horizons consisting of acid sulfate materials, i.e., materials containing soluble acid aluminum and ferric sulfates in concentrations toxic to most common dry-land crops. Such materials have high proportions of exchangeable aluminum, pH (in water) below 4, and may have characteristically pale yellow mottles by basic sulfates of iron, potassium iron or sodium iron sulfates. Some have white mottles of aluminum sulfates.
3) A pseudo-acid (or para) sulfate soil contains one or more horizons with characteristic yellow mottling (basic iron sulfates) that is commonly associated with acid sulfate conditions. The soil does not have a pH below 4 and does not contain free acids or more than 60% exchangeable aluminum.

3.3 Classification and taxonomy of acid sulfate soils

With the notable exception of the FAO legend (1991), most recent morphological classifications distinguish between (actual) acid sulfate soils and potential acid sulfate soils. Soil Taxonomy (Soil Survey Staff, 1990) distinguishes the sulfuric horizon (with a pH in water < 3.5 and jarosite mottles) from sulfidic material (reduced material containing 0.75% or more S and less than three times as much CaCO₃ equivalent) that will become a sulfuric horizon if oxidized.

Potential acid sulfate soils are placed in the Order Entisols, as Sulfaquents (Aquents with sulfidic material within 50 cm of the mineral soil surface), Sulfic Fluvaquents (Fluvaquents with sulfidic material between 50- and 100-cm depth), or Sulfihemists (Histosols with sulfidic material within the 100-cm depth).

Actual acid sulfate soils can be classified as Sulfaquepts (Aquents with a sulfuric horizon that has its upper boundary within 50 cm of the soil surface), Sulfic Tropaquepts (Tropaquepts with jarosite mottles and a pH 3.5 to 4 somewhere within the 50-cm depth, or with jarosite mottles and a pH < 4
in some part between 50- to 150-cm depth), or Sulfic Haplaquepts (comparable to Sulfic Tropaquepts but under a more temperate climate). The distinction between Sulfaquepts and Sulfic subgroups is very useful agronomically in that the former are generally unsuitable for agriculture without costly amendments, whereas the latter can often be made productive with lesser modifications.

Acid sulfate soils that are dominantly organic may be Sulfohemists (Histosols with a sulfuric horizon that has its upper boundary within 50 cm of the surface). Unfortunately, acid sulfate soils with a peaty top soil, which may well be different agronomically from those lower in organic matter, are not separated from the histic subgroups.

Recent proposals to modify Soil Taxonomy regarding acid sulfate soils (Fanning and Witty, 1993) are:

1) Redefine the sulfuric horizon, taking account of acid sulfate soils that do not show jarosite mottles, as a layer > 15 cm thick with a pH in water < 3.8 and evidence that this acidity is caused by oxidation of pyrite (either jarosite mottles, underlying sulfide material or 0.05% or more soluble sulfate);

2) Redefine sulfidic material simply as material that shows a drop of at least 0.5 pH units to < 3.8 during incubation for 8 weeks in moist, oxidized conditions;

3) Provide a new Great Soil Group of Sulfochrepts for acid sulfate soils that are not poorly drained (e.g., on mine
spoil) and a new subgroup of Salorthidic Sulfaquepts for very saline acid sulfate soils.

3.4 Physiography of acid sulfate land in the Bangkok Plain

Thailand is situated between 5° and 21° N Latitude, and between 97° and 106° E Longitude, and covers area about 5.14x10^5 km². Physiographically the country can be subdivided into six regions (Fig. 3.1). The Central Plain, which includes the Bangkok Plain, is a deep syncline filled with sediments. It forms the lower Chao Phraya River basin which is characterized by riverine sediments in its upper reaches and marine and tidal marsh deposits near the coast. The Continental Highlands (200 - 500 m high) and part of the Southeast Coast region belong to the catchment area of the rivers forming the delta of the Bangkok Plain. The Northeast Plateau belongs to the watershed of the Mekong River, which drains into the South China Sea. Peninsular Thailand and the Southeast Coast region are generally hilly and mountainous with altitudes between 200 and 1000 m.

The largest continuous area with acid sulfate soils covering about 8000 km² (0.9 million hectares), is found in the Bangkok Plain between Bangkok and the southern boundary of the Chao Phraya riverine alluvium. Non-acid marine soils occur in a 25 - 40 km wide zone between the acid soils and the coast. Most of the smaller coastal plains fringing the Southeast Coast and Peninsular Thailand have smaller areas
Figure 3.1. Physiographic regions of Thailand (modified from Moormann and Rojanasoonthon, 1972).
with acid sulfate soils, often intimately associated with potentially acid soils and non-acid marine soils.

Acid sulfate soils occur mostly in the Bangkok Plain; hereby the physiographic features of this region will be described briefly. Vacharotayan (1977) divided the Bangkok Plain into three subregions: Old Delta, New Delta, and Fan Complex Area (Fig. 3.2).

The Old Delta is the area located from the northern part of Chainat Province to the Northern part of Ayutthaya Province. The area of this subregion is 5900 km². The altitude gradually decreases from 15 m above mean sea-level at the apex near Chainat to 5 m at Ayutthaya and 1.5 m near the coast. The soils are derived from riverine alluvium but are often underlain by marine and brackish sediments, some of which are potential acid sulfate parent materials.

The New Delta is comprised of two types of areas:

(1) Deltaic High. This area occupies about 2000 km². The elevation is from 3.5 to 5 m above the mean sea-level. The plains are the location of the Bangkok Metropolitan Area and some other provinces in the southeastwards. Soils are of non acid-sulfate marine deposit origin.

(2) Delta Flat. This area has lower elevation than the Deltaic High. It is about 1 to 2 m above the mean sea-level, and during the rainy season the land will occasionally be inundated. The area comprises 11,000 km², of which 80% or 8000 km² is composed of acid sulfate soils.
Figure 3.2. Area of different physiographic regions in the Southern Bangkok Plain (after Vacharotayan, 1977).

The Fan Complex Area develops, forming piedmont topography, along with the marginal parts of the Bangkok Plain, where the Plain merges with the mountain ranges. The total area is estimated to be 18,000 km².
3.5 Genesis of acid sulfate soils

Genesis of acid sulfate soils is composed of two main processes: a geogenetic process and a pedogenetic process. The geogenetic process deals with the formation of pyrite and is termed "sulfidization", whereas the pedogenetic process involves oxidation of pyrite and is termed "sulfuricization" (Pons and van der Kevie, 1969).

3.5.1 Geogenetic process

In the coastal area closed to the estuarine environment, the accretion of sediment takes place under the influences of brackish and marine water. Later, when the sediments are piled high enough, and when the influence of tidal action decreases due to the subsidence of the mean sea-level, some telmatophytic plants such as *Rhizophora*, *Avicennia*, and some other species are able to grow. With the continued flushing of the marine or brackish tide which supply dissolved sulfate, limit aeration, and carry away the carbonate produced, and with the supplementary organic matter from the plants, the secondary pyrite forms slowly and gradually accumulates (van Breemen, 1973b). If the conditions suited for pyrite formation and accumulation are prolonged, the pyrite content in the soil might be as high as 10% of the mass of the soil (van Breemen and Pons, 1978; van Breemen, 1980). van Breemen (1976) also found 160 to 225 cmol. \( \text{SO}_4^{2-} \) kg\(^{-1} \) of soil from air-exposed pyrite sample collected from absolutely non-oxidized pyrite substratum in acid sulfate soils of the Bangkok Plain.
The essential factors for the accumulation of pyrite as summarized by Pons and van Breemen (1982) are:

1) sulfate (e.g., from sea water) is continuously supplied over an appreciable period;
2) iron containing minerals are present in the sediments;
3) metabolizable organic matter;
4) sulfate reducing bacteria, which are practically always present;
5) anaerobic environment;
6) limited aeration for oxidation of all sulfide to disulfide (and/or sulfide to elemental sulfur).

Sulfate is abundant in seawater, thus it will not be a limiting factor in pyrite accumulation. The surface reducing bacteria in the genera *Desulfovibrio* and *Desulfotomaculum* are known to be ubiquitous in marine environments. The clayey sediments of most tidal swamps contain sufficient fine-grained iron oxide for the formation of 2 - 6% pyrite, but iron could be limiting where the soil or sediment is peaty or mainly quartz sand. In tropical seas, suspended sediment is normally low in organic matter for appreciable formation of sedimentary pyrite. The dense mangrove vegetation on tropical tidal marshes can however, supply abundant organic matter. Thus, in mangrove swamps, most of the ingredients for pyrite formation are supplied; and limited aeration will take place depending on tidal influence on soil hydrology.
3.5.1.1 Mechanism of pyrite formation

According to Pons and van Breemen (1982), the formation of pyrite (cubic FeS₂) requires (1) the reduction of sulfate to sulfide under the influence of dissimilatory sulfate-reducing bacteria in an anaerobic environment; (2) the partial oxidation of sulfide to polysulfide or elemental sulfur; and (3) either formation of Fe(II)-monosulfide (from Fe(III)-oxides or Fe-containing silicates and dissolved sulfide) followed by the combination of elemental sulfur and Fe(II)-monosulfide to pyrite, or direct precipitation of pyrite from dissolved Fe(II) iron and polysulfide ion (Roberts et al., 1969; Goldhaber and Kaplan, 1974; Dent, 1986). Whatever the mechanism in operation, formation of pyrite with any Fe(III)-oxide as the source of iron will take place according to the following overall reaction (CH₂O stands for organic matter):

\[
\text{Fe}_2\text{O}_3(s) + 4\text{SO}_4^{2-} + 8\text{CH}_2\text{O} + 1/2\text{O}_2(g) \rightarrow 2\text{FeS}_2(s) + 8\text{HCO}_3^- + 4\text{H}_2\text{O}_1(l)
\]  

[1]

This overall reaction includes reduction of all sulfate to sulfide. Dissolved sulfide reacts rapidly with dissolved ferrous iron or with ferric oxide to form black ferrous sulfide, which is amorphous to X-ray diffraction or gives broad lines of mackinawite (tetragonal FeS). In the presence of oxidants such as O₂ or ferric ion, part of the dissolved or solid sulfide can be oxidized to elemental sulfur. Elemental S reacts with dissolved sulfide to form aqueous polysulfide, which in turn reacts with FeS to form pyrite, FeS₂, either directly or with greigite (cubic Fe₃S₄) as an intermediate
(Rickard, 1975). The pathway involving greigite, which apparently requires atmospheric oxygen, yields framboidal pyrite; whereas the other reaction, in the absence of oxygen, gives non-framboidal pyrite (Sweeny and Kaplan, 1973; Rickard, 1975). The carbonate alkalinity formed by this process is either removed by diffusion or leaching, or is retained by precipitation of CaCO₃ (Hardan, 1973). The interstitial water of marine muds associated with sulfate reduction is often highly supersaturated with calcite, possibly because dissolved organic compounds inhibit crystallization (Berner, 1971). The alkalinity is carried away, leading to a separation of the potentially acid material (pyritic mud) and actual alkalinity (HCO₃⁻), which is mainly absorbed by the vast mass of the oceans. This process is the crucial step that is responsible for the formation of acid sulfate soils.

3.5.2 Pedogenetic process

This process involves profile development, and is mainly implicated in (1) pyrite oxidation; (2) neutralization of acidity; and (3) formation of the products resulting from oxidation and neutralization. The pedogenetic process starts taking place when the geogenetic process is terminated; that is, when the land elevation is high enough to lessen the influence of tidal action that brings about the anaerobiosis. The elevation of the land, relative to the mean sea-level, may be caused by either an increase aggradation of the sediment,
a retreat of the seawater, or a tectonic uplift of the land (van Breemen, 1973b).

3.5.2.1 Pyrite oxidation following drainage

Appreciable aeration of potential acid sulfate soils and subsequent acidification starts only after the water table stays below the upper part of the pyritic zone for several weeks. A prerequisite for such drainage is decreased tidal influence. This is brought about either gradually by natural processes (coastal accretion or a relative decrease in mean sea-level or by tectonic uplift) or more abruptly by man-made activities. Many mangrove areas of the Southeast Asia are still under the tidal influence, acidification takes place in material from the subsoil brought to the surface by the mound building mud lobster, *Thalassina anomale* (Andriesse et al., 1973).

Pyrite is stable only at low redox potential (Eh), i.e., under reduced conditions, and will be oxidized in oxygenated environments. Under natural conditions, dissolved aqueous oxygen attacks pyrite slowly at first, yielding ferrous iron and elemental sulfur:

\[ \text{FeS}_2 + 1/2\text{O}_2 + 2\text{H}^+ \rightarrow \text{Fe}^{2+} + 2\text{S} + \text{H}_2\text{O} \]  \hspace{1cm} [2]

Further oxidation of elemental S to sulfate or sulfuric acid with \( \text{O}_2 \) as oxidant is a slow process:

\[ 2\text{S} + 3\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{SO}_4^{2-} + 4\text{H}^+ \]  \hspace{1cm} [3]

It is likely that equation [2] and [3] are strictly chemical reactions because the pH is near or above neutral, and is not
suitable for Thio- and Ferro-organisms. Arkesteijn (1980) reported that *Thiobacillus thiooxidans* can oxidize elemental sulfur to sulfate under these conditions. *Thiobacillus* bacteria grow optimally at pH 2 to 3.5 (Nordstrom, 1976) although they can survive at pH levels as high as 6 and 7 (Nordstrom, 1982). Whether chemical or biochemical processes, the reaction [3] takes place in acid sulfate soils and causes an increase in acidity. The ferrous iron in reaction [2] can be further oxidized chemically or biochemically to ferric iron. It is noted that *Thiobacillus ferrooxidans* can grow optimally between pH 2.5 and 5.8 (Ivarson et al., 1982). If the pH is high (> 4), ferrous iron will be oxidized and precipitated to ferric hydroxide as follows

\[
\text{Fe}^{2+} + 3 \text{H}_2\text{O} \longrightarrow \text{Fe(OH)}_3 + 3\text{H}^+ + \text{e}^- \quad [4]
\]

If the pH is low enough (< 4), the Fe\(^{3+}\) ions will still be in a dissolved form after oxidation:

\[
\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + \text{e}^- \quad [5]
\]

Dissolved ferric ions in reaction [5], on the other hand, react rapidly with pyrite according to:

\[
\text{FeS}_2 + 2\text{Fe}^{3+} \longrightarrow 3\text{Fe}^{2+} + 2\text{S} \quad [6]
\]

Under most experimental conditions, further oxidation of elemental S is virtually instantaneous according to

\[
2\text{S} + 12\text{Fe}^{3+} + 8\text{H}_2\text{O} \longrightarrow 12\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+ \quad [7]
\]


\[
\text{FeS}_2 + 14\text{Fe}^{3+} + 8\text{H}_2\text{O} \longrightarrow 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+ \quad [8]
\]
Because ferric iron is appreciably soluble only at low pH ( < 4), reactions [6], [7], and [8] are limited to acid environments. In the presence of oxygen, the dissolved ferrous iron produced by these reactions can be further oxidized to ferric iron, and pyrite oxidation can continue. But there is a kinetic restriction: at low pH the oxidation rate of Fe$^{2+}$ by O$_2$ is slow. However, T. ferrooxidans and Ferrobacillus ferrooxidans which are acidiophillic can overcome this barrier, thereby promoting pyrite oxidation (Singer and Stumm, 1970).

Pyrite oxidation in situ is usually much slower due to the rate limiting diffusion of oxygen into the wet pyrite substratum (van Breemen, 1973b; De Richmond et al., 1975). Pons (1965) noted that pyrite in sediment riched with calcium carbonate is oxidized slowly, disappearing over a period of centuries; but that pyrite in acid sulfate soils is oxidized rapidly.

Complete oxidation and hydrolysis of iron to ferric oxide yields 2 moles of sulfuric acid per mole of pyrite:

$$\text{FeS}_2 + 15/4\text{O}_2 + 7/2\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + 2\text{SO}_4^{2-} + 4\text{H}^+$$

[9]

The term sulfuricization has been used to denote these acidification processes (Fanning, 1978).

In addition to the foregoing reactions, in the presence of cations such as K', Na', or H$_3$O', pyrite may be oxidized directly to jarosite or its counterparts according to van Breemen (1973b); van Mensvoort and Tri (1989):
FeS₂ + 15/4O₂ + 5/2H₂O + 1/3K⁺ → 1/3KFe₃(SO₄)₂(OH)₆ + 4/3SO₄²⁻ + 3H⁺

3.5.2.2 Iron sulfide-oxidizing bacteria

Microbes catalyze many reactions including those related to the formation and oxidation of sulfide-ore deposits (Zajic, 1969; Kushner, 1978). Desulfovibrio (e.g., species desulfuricans) and Desulfotomaculum have been mentioned for their important roles in pyrite formations. Some oxidation reactions involving sulfur compounds occur rapidly in vitro at normal temperatures and pressures. The oxidation of some of the more reduced compounds will however, proceed only if they are mediated by certain microorganisms. Most of these microorganisms belong to the Thiobacilli, a group of chemoautotrophic organisms capable of utilizing the energy obtained from the oxidation of H₂S, S⁰, S₂O₃⁻², S₄O₆⁻², SO₃⁻² to SO₄²⁻ for the assimilation of CO₂ (Nor and Tabatabai, 1977).

Three species of Thiobacillus have been isolated from acid mine wastes: T. ferrooxidans, which oxidizes ferrous iron and pyrite as well as sulfur; T. thiooxidans, which oxidizes only sulfur and pyrite; and T. acidophilus, which is a facultative autotroph (grows on either inorganic or organic substrates), oxidizing sulfur but not ferrous iron. Thiobacillus acidophilus cannot oxidize pyrite unless it is in a mixed culture (Guay and Silver, 1975). These bacteria are acidophilic with optimal growth conditions around a pH of 2 to 3 (Kelley, 1985), although they can survive up to pH values as
high as 6 or 7 (Nordstrom, 1982). The *T. ferrooxidans* and *Ferrobacillus ferrooxidans* are able to mediate oxidation of Fe$^{2+}$ to Fe$^{3+}$. Members of the Beggiatoaceae, photoautotrophic bacteria of the Rhodobacteriaceae, and *Sphaerotilus* can also catalyze the oxidation of sulfur compounds, but Thiobacilli are by far the most important group (van Breemen, 1973b).

### 3.5.2.3 Neutralization of acidity

Three different fractions capable of deactivating sulfuric acid have been identified (a) carbonate alkalinity in solution, (b) exchangeable bases, and (c) weatherable minerals.

**a. Alkalinity.** Alkalinity mainly refers to the carbonates of Ca and Mg that have accumulated in the sediments during aggradation that comes with flood water. Calcium carbonate contents are low or nil in most marine sediments of the humid tropics but may be appreciable (frequently higher than 10%) in sediments of arid and humid temperate regions. The acidity from 1% (mass fraction) of pyrite-S is approximately balanced by 3% calcium carbonate. If seawater is entrapped in a sediment and all dissolved sulfate is reduced to sulfide, the increase in bicarbonate would lead to supersaturation with calcium carbonate (Pons et al., 1982).

van Breemen (1973b) has noted that the alkalinity of interstitial waters in non-alkaline soils rarely exceeds 10 meq L$^{-1}$. Hence, at moisture contents up to 100%, dissolved alkalinity can contribute to the neutralization of 1 meq of
acid per 100 g of soil at the most. Seawater has an even lower alkalinity (2 to 2.5 meq L\(^{-1}\)) than most near-neutral ground waters, and cannot be considered as an effective buffering agent, even if copious leaching is applied. Nonetheless, in the eastern part of the Bangkok Plain of Thailand, centuries of seasonal flooding with moderately alkaline water (2 to 5 meq HCO\(_3\)\(^{-}\) L\(^{-1}\); van Breemen, 1973a) have probably increased the pH of the upper horizons of acid sulfate soils to near neutrality (van Breemen, 1973b).

**b. Exchangeable bases.** Active H\(^+\) created by the first stage of pyrite oxidation can be exchanged with exchangeable bases at the soil colloid surfaces. Between 5 and 10 cmol\(_c\) kg\(^{-1}\) of acid in soil is taken up by the exchange complex of typical acid sulfate soils in Thailand where pH drops from 7.5 or 7 to about 5. The total amount of acid taken up by the exchange complex of an acid soil is approximately equivalent to the difference between the CEC at pH 7 and the amount of exchangeable bases at the soil pH (van Breemen, 1973a). For acid sulfate soils of pH 3.5 to 4 from the Bangkok Plain, this amount is about 10 to 30 cmol\(_c\) kg\(^{-1}\) of soil (Sombatpanit, 1970).

**c. Weatherable minerals.** Essentially all alumino-silicates are attacked by acid and release alkaline metals and monomeric silica into solution. If incongruent dissolution takes place, aluminum released from the minerals will be kept as potential acidity in some minerals such as kaolinite, or
basic aluminum sulfate \([\text{Al(OH)}_2\text{SO}_4]\). If monomeric silica polymerizes and precipitates as amorphous silica, the reaction will favor the breakdown of minerals, thereby buffering the acidity. Generally, the layer silicate minerals are concentrated in the clay fraction and because of their large specific surface area, clay minerals can be the important H\(^+\) consumers. Like other common clay soils, acid sulfate soils have been reported containing clay minerals; kaolinite, illite, smectite (montmorillonite, beidellite, nontronite), chlorite, glauconite, and charmomosite (Satawathananont, 1986). In most cases, kaolinite is the predominant clay mineral and is the product of most weathering processes under acid conditions that occurs widely in acid sulfate soils (van Breemen, 1973b). The mechanisms of neutralization of acidity by the minerals can be written as follows:

(i) Congruent dissolution:

\[
\text{M-Al-silicate} + (3+a)\text{H}^+ + b\text{H}_2\text{O} \rightarrow a\text{M}^+ + \text{Al}^{3+} + c\text{H}_4\text{SiO}_4^\circ \quad [11]
\]

(ii) Incongruent dissolution:

\[
\text{M-Al-silicate} + a\text{H}^+ + b\text{H}_2\text{O} \rightarrow a\text{M}^+ + c\text{H}_4\text{SiO}_4^\circ + \text{Al(silicate) residue} \quad [12]
\]

where M = exchangeable bases; a, b, and c are whole integers.

(iii) Incongruent Mg-montmorillonite or smectite to kaolinite:

\[
6\text{Mg-montmorillonite} + 2\text{H}^+ + 23\text{H}_2\text{O} \rightarrow \text{Mg}^{2+} + 7\text{kaolinite} + 8\text{H}_4\text{SiO}_4^\circ \quad [13]
\]
In summary, it appears that the incongruent dissolution of montmorillonite or smectite takes place rapidly. This process is capable of maintaining an equilibrium solution even at high rates of acid formation. If sufficient time is available for dissolved silica to polymerize and precipitate as amorphous silica (which appears to be the case of field conditions) the montmorillonite-kaolinite equilibrium can buffer the pH between 3.5 and 4.5. A much lower equilibrium pH is established if dissolved silica increases beyond the solubility of amorphous SiO₂ which happens upon rapid oxidation associated with high rates of silica release. In the course of months, equilibrium between kaolinite (as well as montmorillonite) and its dissolved constituents is established and can help to maintain pH values between 3.5 and 4 under field conditions. In very acid conditions, kaolinite may break down to buffer a change in pH:

\[
\text{Kaolinite} + 4\text{H}^+ + 2\text{SO}_4^{2-} \rightarrow 2\text{AlOHSO}_4 + 2\text{SiO}_2 + 3\text{H}_2\text{O} \quad [14]
\]

(basic Al sulfate) (amorphous silica)

It should be pointed out that other processes may be involved in maintaining the typical field pH values of 3 to 4. The assemblage jarosite-limonitic goethite will tend to keep the pH at about 3.7. Mica and feldspar are also particularly important because they probably provide much of the K⁺ for jarosite.
3.5.2.4 Products from oxidation and neutralization

The ferrous, hydrogen, and sulfate ions released during pyrite oxidation normally undergo various further reactions in the soil. Protons are largely inactivated by different buffering reactions. Essentially all ferrous iron is ultimately oxidized to ferric iron, which precipitates as jarosite \(\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6\), poorly crystallized goethite, or amorphous ferric oxide. The larger part of the sulfate released during pyrite oxidation, however, remains in solution and is removed from the soil by leaching, and by diffusion into the surface water. The remaining sulfate is partly precipitated, either as jarosite or as the basic aluminum sulfate, \(\text{Al(OH)}_2\text{SO}_4\) (van Breemen, 1973b) and partly adsorbed, mainly by ferric oxides. Under relatively dry conditions, gypsum \((\text{CaSO}_4.2\text{H}_2\text{O})\) can form. Under strongly evaporative conditions, surface crusts of still more soluble sulfates such as sodium alum \((\text{NaAl(SO}_4)_2.12\text{H}_2\text{O})\), tamarugite \((\text{NaAl(SO}_4)_2.6\text{H}_2\text{O})\), pickeringite \((\text{MgAl}_2(\text{SO}_4)_4.22\text{H}_2\text{O})\) and rozenite \((\text{FeSO}_4.4\text{H}_2\text{O})\) have been observed. Under anaerobic conditions, sulfate can be reduced again to sulfide, which may, temporarily, be fixed as \(\text{FeS}\). In very young acid sulfate soils still under tidal influence, this sulfide may even be incorporated in pyrite again (van Breemen, 1973b). The diagenesis of these compounds have effects on morphology and profile development of acid sulfate soils.
a. Jarosite. The general formula of jarosite is \( AB_3(SO_4)_2(OH)_6 \); where \( A = K^+, Na^+, H_3O^+, NH_4^+, Ag^+ \), or \( 1/2Pb^{2+} \) and \( B = Fe^{3+} \) (jarosite) or \( Al^{3+} \) (alunite) (van Breemen, 1973a).

If "A" in a jarosite minerals is \( K^+, Na^+, H_3O^+, \) or \( NH_4^+ \), it should be called as jarosite, natrojarosite, hydronium-jarosite, and ammoniumjarosite, respectively. Most jarosite minerals found in acid sulfate soils are (potassium) jarosite. Jarosite may form according to the reaction:

\[
3Fe(OH)_3^+ + 2SO_4^{2-} + K^+ \rightarrow KFe_3(SO_4)_2(OH)_6
\]  
\[ \text{(15)} \]

(Matijevic et al., 1975)

or

\[
3Fe_2(SO_4)_3 + 1/2O_2 + 11H_2O + 2K^+ \rightarrow 2KFe_3(SO_4)_2(OH)_6 + 5H_2SO_4
\]  
\[ \text{(16)} \]

(Bloomfield and Coulter, 1973; Ivarson et al., 1982).

Typically, jarosite occurs as conspicuous, pale yellow, earthy material as fillings of biopores or as efflorescence on ped faces and pore walls. Individual particles are often smaller than 1 \( \mu \)m and their diameter rarely exceeds 5 \( \mu \)m (Berner, 1971; Ross et al., 1982). van Breemen (1973a) found between 50 to 100% of jarosite contained in most yellow mottles, and sometimes in brown-yellow mottles or even red mottles if these mottles are located close to a jarositic horizon.

Jarosite can be synthesized at room temperature within 1 - 6 months by aeration of a solution of ferrous sulfate \((0.06 - 0.6 \text{ mol L}^{-1})\) and potassium sulfate \((0.01 - 0.1 \text{ mol L}^{-1})\) acidified with \( H_2SO_4 \) to a pH of 0.8 to 1.7 (Brown, 1970).
Ivarson et al. (1979) could detect jarosite after 10 days of aerobic incubation of pyritic mangrove soil. Ivarson (1973) observed the formation of ammonium jarosite within 4 to 10 days in cultures of *T. ferrooxidans* in a medium containing ferrous sulfate. Since the organisms were isolated from natural jarosite samples, it seems likely that they do in fact take place in the formation of jarosite *in situ*.

From synthesis experiments (Brown, 1970) and by the appearance with grain size of jarosite precipitated in acid sulfate soils, Nordstrom (1982) suggested that jarosite can form directly from solution without a precursor solid phase, generally at strong supersaturation faces in association with *Thiobacilli*. In soils, where it is formed more readily than in pure solutions, supersaturation may be maintained for months even when the mineral is present (van Breemen, 1976).

In agreement with theoretical stability relations, jarosite is formed only in acidic (pH 2 to 4), oxidized (Eh > 400 mV) environments. In acid sulfate soils however, it is metastable and will eventually hydrolyze to goethite. Often, brown mottles from acid sulfate soils will give a sharp jarosite X-ray diffraction pattern, indicating that a thin coating of Fe(III) oxide may prevent recognition of jarosite in the field. Hydrolysis is enhanced by leaching and by a supply of bases. Although the yellow color may turn brown within a few months by dialysis (van Breemen, 1976), yellow
jarosite mottles sometimes persist for decades at pH values above 4 in limed soils (Verhoeven, 1973).

Jarosite is stable only under relatively oxidized, acid conditions. Both a decrease in Eh and increase in pH may lead to the disappearance of jarosite

(i) by solution reduction:

\[ \text{KFe}_3(\text{SO}_4)_2(\text{OH})_6 + 6\text{H}^+ \rightarrow \text{K}^+ + 3\text{Fe}^{3+} + 2\text{SO}_4^{2-} + 6\text{H}_2\text{O} \]  \hspace{1cm} [17]

(ii) by hydrolysis:

\[ \text{KFe}_3(\text{SO}_4)_2(\text{OH})_6 + 3\text{H}_2\text{O} \rightarrow \text{K}^+ + 3\text{Fe(OH)}_3 + 2\text{SO}_4^{2-} + 3\text{H}^+ \]  \hspace{1cm} [18]

or

\[ \text{KFe}_3(\text{SO}_4)_2(\text{OH})_6 \rightarrow \text{K}^+ + 3\text{FeOOH} + 2\text{SO}_4^{2-} + 3\text{H}^+ \]  \hspace{1cm} [19]

**b. Iron oxides.** In most acid sulfate soils only part of the iron released as a result of pyrite oxidation (and clay breakdown, e.g., Fe-chlorite) is tied up in jarosite, the bulk being present in free ferric oxides and in the clay mineral beidellite. In acid sulfate soils, Fe(III) oxides may be formed either directly by oxidation of dissolved, solid, adsorbed ferrous iron, or by hydrolysis of jarosite. The first mechanism is dominant in zones where jarosite is absent, for instance, in the upper part of the pyritic substratum and in the A horizon. Ferric oxide mottles in these zones are frequently dark reddish-brown or dark-brown, rather than yellowish-brown as in the B horizon (van Breemen, 1973b).

From the chemical and morphological changes observed in the sequence of acid sulfate soils in Thailand, van Breemen (1973a) indicated that jarosite is formed first and that most
of the ferric oxide in the B horizon of the older soils is formed later by hydrolysis of jarosite. The increase in the prevalence of brown rims around jarosite masses in thin section from shallower depths corroborates this (van Dam and Pons, 1973; Miedema et al., 1974).

At pH values below 6, ferric oxides are incompatible with pyrite, and indeed, most iron oxide is formed at an appreciable distance from pyrite. By contrast, at high pH, as in calcareous pyritic sediments, goethite is often pseudomorphic after pyrite (Miedema et al., 1974).

In the better drained, deeply developed acid sulfate soils, part of the ferric oxides in the B horizon may occur as hematite, giving conspicuous red mottles. It is unlikely that the hematite is formed with ferrihydrite \([\text{Fe}_3\text{H}_6\cdot 4\text{H}_2\text{O}]\) as a precursor (Schwertmann and Cornell, 1991), because conditions favoring ferrihydrite (rapid hydrolysis of dissolved iron at relative high concentrations) are absent in the red mottled B horizons. Perhaps the low pH and periodically dry conditions facilitate transformation of fine-grained goethite, via a solution stage, to the thermodynamically more stable hematite (van Breemen, 1976).

c. Water soluble sulfate. Gypsum has been observed in coastal marine soils over a wide pH range of 3.5 - 7. The upper limit of the calcium activity product in such soil is clearly regulated by precipitation as gypsum. Due to its
fairly high solubility, gypsum is confined to the dryer soils or to those with some supply of calcium carbonate.

The soil solution of acid sulfate soils is generally supersaturated with alunite, the aluminous counterpart of jarosite (van Breemen, 1973b). Alunite has evidently been observed however, in some acid sulfate soils, and is more typical of rock weathering by relatively concentrated sulfuric acid in sheltered or hydrothermal environments.

### 3.5.2.5 Profile development toward maturity

Harmsen and van Breemen (1975) proposed a hypothetical chronosequence (stage A $\rightarrow$ C) of seasonally flooded acid sulfate soils in the Bangkok Plain. Stage A represents an undrained mangrove soil, and B and C illustrate increasingly older and deeper developed acid sulfate soils. When a pyritic soil is drained periodically, e.g., during a dry season, pyrite within 50 cm of the surface can be removed completely in a few decades. Jarosite is formed by oxidation of ferrous sulfate that diffuses upward from the zone where pyrite oxidizes, and accumulates at shallow depths as yellow mottles along pores and cracks (stage B). Jarosite is slowly hydrolyzed to fine-grained goethite in the upper part of the yellow mottled horizon, causing a residue of brown mottles (stage C). In the surface soil, reduction during flooding mobilizes iron, part of which migrates downward. This eventually leads to a lowering of ferric oxide near the soil surface (stage C). Thus, as the soils become older (in terms
of pedological maturity, not absolute age) and better drained, the different horizons are found at a progressively greater depth. For example, while the acid sulfate soils from inland parts of the Bangkok Plain and the Me Kong Delta, especially those in the Plain of Reeds, developed in sediments of probably the same age, most of the soils from Vietnam are more poorly drained and hence less developed and younger than those from Thailand.

Due to low decomposition rates under acidic conditions, acid sulfate soils often have a distinctly higher organic carbon content in the surface horizon than comparable non-acid marine soils (Kawaguchi and Kyuma, 1969). Still lower rates of organic matter decomposition prevail in acid sulfate soils in continuously wet equatorial climates. Such soils often have a peaty surface layer as in Western Malaysia (Chow and Ng, 1969) and southern Kalimantan (Driessen and Soepraptohardjo, 1974).

Peaty surface horizons are also found in poorly drained acid sulfate soils in monsoon climates as in Kerala state, India (Rao et al., 1975), the Plain of Reeds, Vietnam (Dent, 1986), and Southern Peninsular of Thailand (Krisornpornsan, 1991). Acid sulfate soils developed in highly organic pyritic sediments sometimes lack the conspicuous yellow mottles, probably because they are generally too reduced to permit the persistence of jarosite (Kosaka, 1971).
3.6 Problems of acid sulfate soils to rice production

The problems concerning acid sulfate soils used for rice production include 1) adverse effect of H⁺, 2) aluminum toxicity, 3) iron toxicity, 4) phosphorus deficiency, and 5) low base status.

3.6.1 Adverse effect of H⁺

The direct adverse effect of H⁺ on plants have been observed at an acidity stronger than pH 3.5 - 4. The probability of soil acidity directly resulting in plant growth problems on some acid sulfate soils has already been reported (Moormann, 1963; Brinkman and Pons, 1973). Rice grown in solution culture is found also to be affected directly by H⁺ at pH below 3.5 to 4 (Ponnamperuma et al., 1973; Thawornwong and van Diest, 1974).

Occasionally, in young acid sulfate soils (Sulfaquepts) and rapidly oxidized potential acid sulfate soils (Sulfaquents), pH levels as low as 3 or even lower can be found. In addition, pH values of approximately 1 to 2 have been observed in oxidized horizons of acid sulfate soils (Tanaka and Yoshida, 1970; van Breemen and Pons, 1978). The H⁺ injury can be eliminated by raising pH above 4.

3.6.2 Aluminum toxicity

Ponnamperuma (1972) reported that aluminum in acid sulfate soils becomes more soluble at a low pH. At a pH lower than 4.4, a high concentration of aluminum in the soil solution is found to be toxic to rice plants. Cate and Sukhai (1964)
reported that the toxic effects of Al on the growth of rice seedlings appeared when Al concentrations were greater than 1.2 mg L\(^{-1}\). Young rice seedlings growing in pH 3.5 to 5.4 solutions were adversely affected by 0.5 - 2 mg L\(^{-1}\) dissolved Al, and 3 to 4 week-old plants were suffered from more than 25 mg Al L\(^{-1}\) (Tanaka and Navasero, 1966a; Thawornwong and van Diest, 1974). The death of rice plants grown on some acid sulfate soils of Vietnam which contained 68 mg kg\(^{-1}\) of dissolved Al was attributed to Al toxicity (Nhung and Ponnampemura, 1966).

Regardless of the type of acid sulfate soils, such toxic levels occur at soil pH below 4.5 - 5.0 for seedlings, and below 3.5 - 4.2 for older plants. These critical values however, depend on other factors. Phosphate, for instance, counteracts Al toxicity, partly due to coprecipitation of Al and P outside the plants and in the roots (Tanaka and Navasero, 1966b; Rorison, 1973; Attanandana, 1982). Tanaka and Navasero (1966a) reported that in a culture solution, the critical level of Al was 25 mg L\(^{-1}\) for normal rice plants, 15 mg L\(^{-1}\) for P-deficient plants, and no toxic symptoms were observed even at concentrations of Al as high as 40 mg L\(^{-1}\) in high P treated solutions. The low availability and high fixation of P in acid sulfate soils (Hesse, 1963; Watts, 1969) may therefore aggravate Al toxicity (van Breemen and Pons, 1978).
High Al levels affect cell division, disrupt certain enzyme systems, and hamper uptake of P, K, Ca and several essential cations (Rorison, 1973). Aluminum can also disrupt the activities of proteinaceous enzymes located in the cell wall. The harmful effects of Al are more pronounced in the root. Aluminum concentrations as low as 1 to 2 mg L⁻¹ markedly retard the growth of rice roots (Cate and Sukhai, 1964). Symptoms of Al toxicity to rice plants may be observed initially by interveinal orange-yellow discolorations of the tips followed by brown mottling (Yoshida, 1981; Tadano, 1985). Because Al contents in the plant do not necessarily reflect aluminum toxicity, the disorder is easily overlooked (van Breemen and Pons, 1978).

Aluminum toxicity is predominant when soils are unsaturated and just after flooding. After prolonged submerging when pH rises, Al will precipitate, and the toxicity is eliminated. In acid sulfate soils which contain low reactive reducible Fe and low easily decomposable organic matter, pH rises slowly, and Al toxicity may persist for several weeks. Broadcast rice, which grows for 2 to 4 months as dryland crop before flooding starts, as in the Bangkok Plain, may suffer from Al toxicity (Jugsujinda et al., 1978).

Aluminum injury can be eliminated by raising the soil pH above 5.0 by liming or by keeping the soil submerge for several weeks before planting (Ponnampuruma et al., 1973) or by leaching (van Breemen and Pons, 1978). Many researchers
have overcome Al toxicity by liming or applying heavy doses of phosphate (Nhung and Ponnampara, 1966; Jones and Fox, 1978; Attanandana, 1982). Organic residues which accelerate soil reduction after flooding could eliminate Al injury.

3.6.3 Iron toxicity

In acid sulfate soils, iron toxicity is an important growth limiting factor (Tanaka and Yoshida, 1970; Ponnampara et al., 1973). Iron toxicity has been observed in soils with pH below 5.8 when aerobic, and pH below 6.5 when anaerobic (van Breemen and Moormann, 1978). Reported toxic levels of Fe in culture solutions vary from 10 to 20 mg L\(^{-1}\) to more than 500 mg L\(^{-1}\) (Ishizuka, 1961; Tanaka et al., 1966). The wide ranges may be due to differences in criteria used for toxicity (van Breemen and Moormann, 1978).

At least three criteria have been used to define toxic levels: plant growth, degree of bronzing, and Fe content of the plants. Ishizuka (1961) found that rice growth increased as Fe\(^{2+}\) concentrations in a culture solution increased from 0 to 0.1 mg L\(^{-1}\), but the growth was adversely affected at concentrations above 10 mg L\(^{-1}\). Bronzing symptoms generally appear at higher Fe concentrations: 30 to 80 mg kg\(^{-1}\) in pot experiments with soils from Sri Lanka (Mulleriyawa, 1966), 100 to 500 mg L\(^{-1}\) in culture solutions (Tanaka et al., 1966), and 300 to 400 mg L\(^{-1}\) in soils well supplied with nutrients (IRRI, 1972).
Likewise, the Fe content in plants of a given variety grown at a given time and place usually correlates well with the degree of bronzing (Inada, 1965; Ota, 1968); but Fe contents in plants of different varieties, all moderately affected by bronzing, may vary from 110 to 1100 mg Fe kg\(^{-1}\) (Jayawardena et al., 1977; Ismunadji and von Uexkull, 1977). Furthermore, because apparently healthy plants may contain more than 1000 to 1500 mg Fe kg\(^{-1}\) (Ota, 1968; Tanaka and Yoshida, 1970), it is probably impossible to define a generally applicable critical Fe content in rice tissue. To confirm suspected Fe toxicity, a comparison of the Fe contents in leaf blades of affected and healthy plants from the same field may be most useful (van Breemen and Moormann, 1978).

Iron toxicity in the soil is attributed to a high concentration of ferrous iron in the soil solution. The concentration of Fe\(^{2+}\) normally increases in a soil after flooding due to reduction of ferric oxide by organic matter. A rapid rise in Fe\(^{2+}\) is favored by a low initial soil pH, active iron oxide, the absence of compounds with a higher oxidation state than ferric oxide (Ponnampерума, 1972), factors stimulating anaerobic microbial activity such as an abundant supply of easily decomposable organic matter, and a high nutrient status (van Breemen and Moormann, 1978). In most soils, Fe\(^{2+}\) increases to 100 - 600 mg kg\(^{-1}\) in the first 2 to 10 weeks after flooding and later decreases to levels between 50 and 100 mg kg\(^{-1}\) in a few weeks. In acid sulfate soils the Fe\(^{2+}\)
peaks after several months, reaching 100 - 4000 mg kg\(^{-1}\) (van Breemen and Moormann, 1978).

Reduction of iron oxide to Fe\(^{2+}\) consumes H\(^+\) and increases pH (Ponnampeteruma, 1972):

\[
\text{Fe}_2\text{O}_3 + 3\text{H}^+ \rightarrow 2\text{Fe}^{2+} + 3\text{OH}^{-}
\]  

[20]

In most acid soils, pH normally reaches between 6.4 and 7.0 within 2 to 5 weeks after flooding. But in acid sulfate soils which are low in easily decomposable organic matter, low in active iron oxide, and have an extremely low pH, reduction of iron oxide is minimal. Therefore, the soil pH increases slowly (van Breemen and Moormann, 1978).

In Sulfaquents and Sulfaquepts, in which pyrite is found at a shallow depth, a considerable amount of Fe\(^{2+}\) may be derived from the oxidation of pyrite. The Fe\(^{2+}\) ions (or in the form of ferrous sulfate) later diffuse upward to the oxidized layers and surface soils. Some of the Fe\(^{2+}\) will be slowly oxidized to Fe\(^{3+}\). Although some Fe precipitates in oxidized layers and as a film on the surface soils, large amounts of iron as Fe\(^{2+}\) and Fe\(^{3+}\) still exist in aqueous form. In such situations Fe toxicity may result. De Guzman (1965) showed that Fe(III)-EDTA apparently induced bronzing only at 5 to 10 mg L\(^{-1}\) of Fe\(^{3+}\). Iron toxicity is normally found in Sulfaquepts, and sometimes in Sulfic Tropaquepts.

The critical Fe level in growth media required to produce bronzing differs with the age, variety, and possibly with the nutritional status of the plants. Tadano (1970, 1975) showed
that rice roots have a built-in protective mechanism which enables them to exclude an excessive amount of Fe\(^{2+}\). The Fe excluding power is weakened in plants deficient in P, Ca, Mg, Mn, and especially in K. On the other hand, if a high level of Fe is present in the soil solution, the uptake of P, K, and Mn will also be adversely affected. A high salinity due to NaCl or MgCl\(_2\) is known to decrease the oxidizing power of rice roots and thus enhance Fe toxicity. However, in the case of acid sulfate soils, the extremely low pH would weaken the protective mechanism of rice roots against the uptake of an excessive amount of Fe.

In some acid sulfate soils, rice well supplied with nutrients apparently suffers from Fe toxicity only if dissolved Fe\(^{2+}\) is higher than 300 to 400 mg L\(^{-1}\). It is not clear whether varietal differences in tolerance for Fe\(^{2+}\) are due mainly to exclusion of Fe in the oxidizing rhizosphere, to reduced translocation of Fe, to tolerance for high Fe levels in the plant tissue, or to a combination of these factors (Jayawardena et al., 1977; Tadano, 1985).

Ameliorations of Fe toxicity include liming, drainage and leaching, presubmergence, prevention of deep drainage, and the use of tolerant rice varieties. Liming suppresses a high concentration of Fe by raising pH, thereby precipitating Fe. Presubmergence tends to hasten the period of decline after reaching peak concentration. The addition of fresh organic matter has been found to shorten the period of high Fe\(^{2+}\)
content (IRRI, 1976). The prevention of deep drainage will maintain the watertable above the pyritic layer, thereby minimizing pyrite oxidation. The use of tolerant plants seems to be economical for Fe-toxic soil.

### 3.6.4 Phosphorus deficiency

In acid sulfate soils, P is strongly fixed in unavailable forms such as iron and aluminum phosphate or phosphate adsorbed to clay surfaces. With time, the phosphate may be converted to the more insoluble ferric phosphate and even occluded with iron oxide (Hesse, 1963). At low soil pH, iron and aluminum play a major role in phosphorus fixation (Yuan et al., 1960).

Patrick and Khalid (1974) observed that in an aerobic acid soil, P coprecipitates with Fe and Al and is occluded with iron oxide; under reducing conditions, some of the iron and aluminum phosphate becomes available, but the degree of mobilization by flooding will gradually be reduced by aging and crystallization of the oxides. Acid sulfate soils containing low available P, showed a slight increase in P availability with flooding (Pattrick et al., 1985).

Attanandana and Vacharotayan (1982) reported that Sulfic Tropaquepts required a high level of applied P, and the Rangsit very acid soil, with or without lime, was the only soil not responding to any fertilization in the absence of P. When the initial soil pH is 4.2 to 4.5, the response to lime is often low and rarely significant; phosphate application
alone at 50 to 100 kg P$_2$O$_5$ ha$^{-1}$ gives a dramatic positive effect even on unlimed acid soils (pH 3.6 - 4.2) (van Breemen and Pons, 1978). The very acid sulfate soils of the Bangkok Plain show good responses to P and lime (Attanandana, 1982). Rock phosphate with a high level of citrate solubility proved to be a good source of P for rice yields in acid sulfate soils of Thailand (Engelstad et al., 1974). In addition, residual effects of rock phosphate lasted for five consecutive crops in Thailand (Jugsujinda and Suwannawoang, 1973).

3.6.5 Low base status

Attanandana and Vacharotayan (1982) reported that in an extremely acid sulfate soil in Thailand, extractable K and Ca are low, whereas extractable Al is very high. In a potential acid sulfate soil of Senegal, exchangeable Ca, K, and Mg were found to be 2.6, 0.7, and 8.2 cmol$_c$ kg$^{-1}$ of soil, respectively (Toure, 1982). The quantities of exchangeable Ca and Mg found in the surface layer of acid sulfate soils in Thailand were 3.5 to 5.0 and 3.0 to 3.3 cmol$_c$ kg$^{-1}$, respectively (Attanandana, 1982).
References


CHAPTER 4
Aluminum toxicity and tolerance of plants to acid soils

4.1 Aluminum toxicity symptoms and mechanisms of plant tolerance

4.1.1 Physiological and biochemical effects of aluminum toxicity

Aluminum toxicity is probably the most important growth-limiting factor for plants in strongly acidic soils (Foy, 1988). The problem is particularly severe below pH 5.0, but has been reported to occur as high as pH 5.5 in acid sulfate soils (Cate and Sukhai, 1964). The critical soil pH at which Al becomes toxic depends upon many factors, including the predominant clay minerals, organic matter levels, concentrations of other cations, anions and total salts, and particularly, the plant species or cultivar (Kamprath and Foy, 1985).

Symptoms of Al toxicity are remarkably similar for most plants. They are most pronounced on the root system, where roots tend to be shortened and swollen. The entire root system has a stubby appearance because lateral-root growth is inhibited to a greater extent than primary-root growth (Foy, 1974). With increasing severity of Al toxicity, roots become sparse, shorter, and more swollen, and fine branching vanishes.
Moderate levels of Al toxicity show no characteristic foliage symptoms and tend to go undetected. Under severe Al stress, plant tops are stunted and are often indistinguishable from P-deficiency symptoms (Foy, 1984). Although Al phytotoxicity is not readily recognizable in the field by foliage symptoms, it can be readily diagnosed by the appearance of damaged roots.

Despite a large body of literature documenting Al toxicity and tolerance, the physiological basis remains elusive (Fageria et al. 1988; Marschner, 1991). Toxicity appears to be the result of several interactions, and there is no consensus on the mechanisms of Al toxicity in higher plants. To some extent, Al clearly has a deleterious effect on numerous physiological aspects of the affected species. The inability to use phosphate in the presence of Al appears to contribute to toxicity (Foy and Campbell, 1984), probably as a result of the formation of aluminum phosphate complexes within the tissue. Exposure to Al also results in the reduction of free Mg and Ca in plant tissue. It has been shown in different upland rice cultivars that under Al toxic conditions, Mg levels are reduced below those critical for tissue survival (Fageria and Carvalho, 1982); Ca uptake was reduced by as much as 90% (Fageria, 1985). It has been hypothesized that Al rhizotoxicity is related to disruption of membrane function. Several biochemical effects are probably due to changes in the structure and function of the root cell plasmalemma (Hecht-
Buchholz and Foy, 1981). Depending on the pH, Al can bind to membrane proteins and lipids (Foy and Campbell, 1984). Aluminum can also participate in the formation of cross-links between proteins and pectins within the cell wall, making the wall more rigid. These interactions would have a deleterious effect on membrane integrity. Wheat roots that exhibit severe symptoms of Al toxicity however, have an undiminished capacity to extrude protons, suggesting that these membranes are intact and ATP synthesis is sufficient to supply the proton-translocating ATPases (Kinraide, 1988). It has been reported that abnormal root growth is the result of disturbed mitotic processes (Marschner, 1986). Aluminum is particularly concentrated in the nucleus (Foy et al., 1978). The cell cycle is inhibited, probably at the level of DNA replication where Al inhibits the synthesis of DNA (Foy, 1974, 1983). Kinraide and Parker (1987) suggest two categories of Al phytotoxicity: (1) binding or precipitation on cell surfaces, thereby interfering with membrane function, and (2) combining with biologically important ligands such as DNA. Most of the effects of phytotoxic Al are manifested in root growth and function (Foy, 1983; Taylor, 1988). Root elongation rate is the most commonly used indicator of plant response to Al (Hue et al., 1986). Susceptibility to Al toxicity appears to be the greatest in young seedlings and decreases as plants continue to grow. Roots of rice (Thawornwong and van Diest, 1974) and alfalfa (Kapland and Estes, 1985) seedlings have been shown to
be more sensitive to Al than roots of the mature plants. At 2 mg L\(^{-1}\) in nutrient solution, Al was lethal to rice seedlings but had no effect on dry-matter yields when added to 18 day-old plants (Thawornwong and van Diest, 1974).

4.1.2 Mechanisms of plant adaptation and aluminum tolerance to acid soils

As high Al concentration in acid soils is a key factor limiting crop production, research emphasis has been on mechanisms of Al tolerance. Plant species and genotypes within species show great differences in Al tolerance (Foy, 1988; Wright, 1989; Foy, 1991). Genetic control of Al tolerance has been reported for a number of crops, including maize (Zea mays L.), wheat (Triticum aestivum L.), sorghum (Sorghum bicolor L. Moench), and rice (Oryza sativa L.) (Fageria et al., 1988). This tolerance can be exhibited in terms of better root and shoot growth and more efficient utilization of nutrients.

There is currently no unified view on the physiological and biochemical basis of Al tolerance in crops. Solution studies with well defined conditions grouped tolerance mechanism into two categories: external and internal (Marschner, 1991). External or exclusion tolerance mechanisms occur in the root apoplasm (portions external to the cell membranes) which prevent Al from entering the symplasm (portions within the cell membranes but excluding the vacuoles) and from reaching sensitive metabolic sites. Internal Al tolerance mechanisms involve Al passing into the symplasm and detoxification,
immobilization or changes in metabolism occurring at that point (Marschner, 1991).

Exclusion mechanisms may include immobilization of Al at the cell wall, selective permeability of the plasma membrane, plant-induced pH changes in the rhizosphere, and exudation of chelating ligands (Marschner, 1991). A majority of Al in plant roots is bound to the cell wall (Schaedle et al., 1986). Plant-induced pH increases in the rhizosphere have not consistently been associated with Al tolerance (Taylor, 1988). Organic chelating agents exuded from plant roots or in the mucilage at the root cap could detoxify Al. A large and continuous supply of chelating agent would however, be needed to depress aluminum activities (Al\(^{3+}\)) and this would impose a considerable energetic cost to the plant (Marschner, 1991).

Chelation of Al by organic acids or proteins in the cytosol, Al compartmentation in the vacuole and evolution of Al-tolerant enzymes have been proposed as internal tolerance mechanisms (Marschner, 1991). Thus, it is not surprising that Al-tolerant plants often produce large amounts of organic acids (Mengel and Kirkby, 1982). Al-tolerant barley maintains high concentrations of organic acids in roots (Foy et al., 1987). In maize roots exposed to Al, there is a large increase in organic acids, especially malate, citrate, and trans-aconitate (Suhayda and Haug, 1986). In suspension cultures, the toxic effect of Al decreased greatly after addition of acid fraction of the conditioned media from tolerant cells.
(Ojima et al., 1984). This fraction contained four different organic acids, primarily citrate. Moreover, the toxic effects of Al could also be reduced by addition of citric or malic acid to the cells. Therefore, at least in cell culture, tolerance may be related to the production and release of organic acids by the cells (Bennett and Breen, 1991).

4.2 Tolerance of green manure crops to acid soil conditions

Green manure crops can be leguminous as well as nonleguminous and can be grown in situ or brought from outside as cutting of trees and shrubs. In Thailand, leguminous green manures are more common.

4.2.1 Type of green manures for in situ incorporation

Leguminous green manure crops contain a relative high N content (2.5 - 4.5% of dry matter), and they can grow well on adverse soils of low organic matter, high or low pH, and can subsequently help to improve the fertility status of the problem soils (Singh et al., 1991).

Recently, several experiments have been conducted on green manuring crops in Thailand (Thawornmas et al., 1977; Donsae et al., 1981; Sukthumrong et al., 1986). A promising green manure should have the following characteristics: fast growth, a large biomass, well developed root system, tolerant of drought, alkalinity and acidity, easy incorporation, and rapid decomposition to yield a large amount of plant nutrients (Chinapun, 1982). Sunn hemp (Crotalaria juncea), green gram
(Vigna radiata), cowpea (Vigna unguiculata), pigeon pea (Cajanus cajan), mimosa (Mimosa invisa), stylo (Stylosanthes humiles), leucaena (Leucaena leucocephala), and Sesbania (Sesbania spp) are the most widely grown green manures in Thailand.

Sunn hemp is a root-nodulating green manure that commonly grows in low rainfall and limited soil moisture areas but less tolerant of salinity and acidity (Sratongkam, 1976). Naklang et al. (1980) found that sunn hemp used as a green manure increased rice yields. It was also considered as a possible fodder crop. It could produce significant forage when planted in bunded rice fields with one buffalo plowing after rice harvest (Shelton, 1976). Many insect pests, however, especially pod borers, cause marked reductions in both forage and seed yields (Phisikul et al., 1980). Cowpea, at present, not a major crop in Thailand, performs well as a short season crop, with better drought resistance than mungbean (Phaseolus aureus) or soybean for the uncertain period before the monsoon of Northeastern area. Its seed has satisfactory flour-milling quality, and values both as food and as green manures by possessing higher water-use efficiency in terms of dry matter and N production (Wallis and Byth, 1988).

Sesbania species are good green manure crops because of their vigorous growth, adaptation to various soil conditions, and ability to enhance soil fertility by transferring fixed N to the main crop (Evans and Rotar, 1987). Sesbania favors the
moist tropics; many species show exceptional tolerance for waterlogged soils, which appears in part through their ability to nodulate. Stem nodulation species, *Sesbania rostrata*, is potentially an important green manure crop preceding rice. *S. bispinosa*, *S. grandiflora* and *S. sesban* have been grown widely.

*Sesbania bispinosa* (Jacq.) W.F. Wigh is a shrubby annual or short-lived perennial that can grow to 4 - 5 m tall. It is also known as *S. aculeata* (Willd.) Poir. and as *S. cannabina* (Retz.) Poir., and by the common name dhaincha (Duke, 1981). Dhaincha has thick glabrous stems, large (35 cm) pinnate leaves, yellow flowers, and long (25 cm) curved pod. It is self-fertile and seeds freely. It is a multipurpose shrub; the wood and leaves are used for poles, fiber, fodder, and green manure. It is adapted to wet areas and heavy soils. It is viewed as a marsh plant able to produce floating roots with a spongy aerenchyma, and is also said to withstand drought, with rainfall as low as 500 mm in the growing season.

*Sesbania bispinosa* is grown widely as the short-duration legume before or after rice in the Bangkok Plain and some areas of the Northeast region (Hongpan, 1962; Plangkool, 1980). Seeds are sown at the onset of the monsoon; 2-to 3-month-old plants are incorporated before rice is transplanted. Its rapid growth resulted in N accumulation of 80 kg ha\(^{-1}\) in 30 d and 230 kg N in 60 d at Khon Kaen (Chandrapanya et al., 1982). Evans and Rotar (1987) reported yield averages of 26
tons fresh foliage ha\(^{-1}\) from growth periods averaging 75 d. Its yields greatly exceed those of other green manure crops, such as crotalaria, mungbean and pigeon pea. Its leaves are pinnate, averaging about 38 cm long, with 20 - 50 leaflets, 1.2 - 2.5 cm long, per leaf. The leaflets degrade rapidly in moist soil and release 50% of their N contents within 4 weeks of incorporation (IRRI, 1985).

Among the stem-nodulating legumes, *Sesbania rostrata* and *S. cannabina* have received particular attention. These are characterized by profuse stem nodulation, and faster growth than most root-nodulating legumes. Also, *S. rostrata* exhibits two unique properties: it has high N\(_2\)-fixing potential (measured as fixing 200 kg N\(_2\) ha\(^{-1}\) in 50 days) and it has the ability to nodulate and fix N even with high rate of combined N in the soil (about 200 kg N ha\(^{-1}\)). That *S. rostrata* can assimilate both soil and atmospheric N constitutes a significant advantage (Dreyfus et al., 1985). The stem-nodulating legumes usually show a high sensitivity to climatic variations, particularly to temperature and photoperiod (Rinaudo et al., 1988). Besides being a green manure, sesbania can be grown as a forage crop and as human food. In Thailand, flowers of *S. grandiflora* and *S. roxburghii* are an accepted vegetable (Arunin et al., 1988).

*Leucaena* has been the most successful species because of its deep rooting, however it is slow to establish and has poor growth on acid soils. Potential of *Leucaena* with wetland rice
in Thailand is limited because it does not tolerate flooding, and must be cut off aggressively to avoid shading (Arunin et al., 1988). Species of *Sesbania* (mostly *S. sesban*) appear promising, with yields and reasonable leaf retention over the dry season, and use for *in situ* green manure as well as GLM (Topark-Ngarm and Gutteridge, 1985).

Green leaf manures (GLM) are preferred when raising green manures *in situ* is not possible, especially in areas with limitations such as lack of irrigation water and due to loss of main crop growing season. Woody species of the genera *Leucaena* and *Sesbania*, which are widely used in food crop systems, are the important GLMs. *Leucaena* is of interest primarily as animal fodder (Brewbaker, 1985, 1987b). It is planted widely for fuel and post wood, increasingly is being studied as a source of pulpwood and timber, is used as nurse trees with plantation crops, and is planted for shade or soil amelioration. *Leucaena* herbage yields generally exceed those of other shrubby tropical legumes and are comparable to those of the best herbaceous legumes. They range from 40 to 80 tons fresh weight ha\(^{-1}\) when moisture is not limiting (Brewbaker, 1987a). Yields are reduced to 20 - 50 tons ha\(^{-1}\) in the seasonally dry tropics. Yields are optimized with a harvest cycle of 2 - 4 months. Other variables affecting yield include variety, cutting height, and plant densities.
4.2.2 Sesbania tolerance to adverse conditions

4.2.2.1 Flood tolerance

*Sesbania* species are known for their ability to withstand flooding. In China, sesbania survived for 15 - 20 days in water at 5 - 30 cm deep (Evans and Rotar, 1987).

Tolerance of sesbania to flooding develops after the seedling stage. Although a few centimeters of standing water aids germination of *S. bispinosa*, the seedlings appear to need several weeks of nonflooded conditions before they can readily withstand flooding. The basis for flood tolerance in sesbania is the development of aerenchyma, a spongy tissue having enlarged cell with large intercellular spaces. This development allows the plant to avoid anoxia in the root zone.

In a study of the performance and yields of four *Sesbania* species under flooded (30 cm deep) and upland conditions, the ability to tolerate flooding was increased in the order *S. rostrata* > *S. aculeata* > *S. cannabina* > *S. speciosa* (Arunin et al., 1987).

4.2.2.2 Salt tolerance

Many *Sesbania* species are tolerant of saline and alkaline conditions. African species of sesbania are segregated in habitat according to the degree of salinity in the edaphic environment. This tolerance may be related to water requirement; species with greater adaptation to drought might be expected to encounter increasing salinity as soils
dry out or as seasonal surface water evaporates (Evans and Rotar, 1987).

Singhabutra et al. (1987) studied the effect of salinity levels - 0.56, 1.89, 4.40, 5.64, and 6.18 dS m\textsuperscript{-1} - on Sesbania spp. As salinity increased, plant height, fresh weight, and number of nodules decreased in the order of S. speciosa > S. cannabina > S. rostrata > and S. aculeata.

4.2.2.3 Acid tolerance

Plants which are able to colonize problem soils are important in stabilizing and reclaiming such lands. The ability of Sesbania species to grow in a wide range of soil conditions has resulted in an expanded range of adaptability and utility compared to many other legumes.

Sesbania species have been recognized for their tolerance to soil salinity and flooding; some also grow well in acid soils. Sesbania cannabina or S. bispinosa, known for its tolerance of soil alkalinity in India, appears tolerant of soil acidity. The crop was grown as a green manure on acidic tea-growing soils in Assam (Patel, 1966). Sesbania sesban is reportedly grown successfully on acid sulfate soils in Viet Nam. Tran phuoc Duong of Cantho Agricultural College, Viet Nam, in an illustrated lecture given at the University of Hawaii in 1983, presented a photograph of Sesbania species growing in a soil crusted with aluminum salts, and stated that Sesbania was generally sown at the end of the monsoon season.
(Evans and Rotar, 1987). No research has been carried out in Thailand on *Sesbania* tolerance to soil acidity.

Tolerance diversity of *Sesbania* was demonstrated by Yost et al. (1985), who grew *S. grandiflora* across a pH gradient established by liming a manganiferous Oxisol in Hawaii. One annual variety of sesbania used (USDA PI 180050) appeared quite sensitive to low pH and the associated high levels of available soil Mn. This variety has been found to be different from other species accessions received as *S. cannabina* or *S. bispinosa* (Evans, 1983). Although amounts of N accumulated in *S. grandiflora* were low relative to the more rapidly growing annual crops, it showed a tolerance to low pH comparable to that of *Crotalaria juncea*.

A group of *Sesbania* species were tested for response to lime applied to two acid soils (Evans, 1986). The 28 accessions grown in pots showed wide diversity in response to an aluminous Ultisol pH 3.8 - 5.0 and a manganiferous Oxisol pH 5.2 - 6.0. Yield increases due to the lime additions averaged approximately 80% over no-lime treatments in each soil. Yield variation among accessions was manyfold in the Mn-dominated soil, varying by a factor of 40 at both pH levels. Variation was much less in the Al-dominated soil, by factor of 2.3 at both pH values. The results suggested that *Sesbania* cultivars could be selected to provide good yields on acid soils.
References


Sukthumrong, A., S. Chotechaungmanirat, J. Chancharoensook, and V. Verasan. 1986. Effect of green manure-chemical fertilizer combinations on soil fertility and yield of


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CHAPTER 5

Chemistry of acid sulfate soils and aluminum detoxification by organic amendments

5.1 Chemistry and mineralogy of aluminum, iron and sulfur in acid sulfate soils

5.1.1 Acid development by oxidation of pyrite

The fine-grained pyrite typical of tidal sediments oxidizes readily upon exposure to the air, giving Fe(II) sulfate and sulfuric acid:

\[ \text{FeS}_2 + \frac{7}{2} \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+ \quad [1] \]

Sulfite forms as an intermediate, and there are indications that appreciable amounts of sulfur are sometimes removed as gaseous sulfur dioxide from young acid sulfate soils (van Breemen, 1976). Complete oxidation and hydrolysis of iron to Fe(III) oxide yields 2 moles of sulfuric acid per mole of pyrite:

\[ \text{FeS}_2 + \frac{15}{4} \text{O}_2 + 7/2\text{H}_2\text{O} \rightarrow \text{Fe}^{3+} + 2\text{SO}_4^{2-} + 4\text{H}^+ \quad [2] \]

The term "sulfuricization or hyperacidity" has been used to denote these acidification processes (Fanning, 1978). Oxidation of Fe(II) to Fe(III) by O\(_2\) is slow \textit{in vitro} but the reaction rate is greatly enhanced by the chemoautotrophic organism \textit{Thiobacillus ferro-oxidans}. Pyrite is oxidized more rapidly by dissolved Fe(III) than by O\(_2\), according to:

\[ \text{FeS}_2 + 14\text{Fe}^{3+} + 8\text{H}_2\text{O} \rightarrow 15\text{Fe}^{2+} + 16\text{H}^+ + 2\text{SO}_4^{2-} \quad [3] \]
Because a low pH and the activity of *T. ferrooxidans* are required to maintain appreciable concentrations of dissolved Fe(III), these conditions also promote pyrite oxidation (van Breemen, 1988). The importance of catalytic effect of the Fe(III)-*T. ferrooxidans* couple is well established for acid mine drainage, where the pH commonly drops below 3 (Taylor et al., 1984). *T. ferrooxidans* is commonly present in acid sulfate soils (Bloomfield and Coulter, 1973), but since the pH of the soil rarely falls below the 3 - 3.5 range, its importance for the oxidation of pyrite may be limited.

Thus, pyrite oxidation involves a series of complex processes, many of which are potentially rate determining. The rate of pyrite oxidation in the field is simply determined by the rate of O$_2$ supply (van Breemen, 1976). This has an important practical consequence: soil acidification due to pyrite oxidation is slower when pyrite occurs at an appreciable depth below the soil surface (i.e., below 50 cm) than at very shallow depth or when pyritic soils is dug up and is directly exposed to the air.

### 5.1.2 Mineralogy and oxidation products of pyrite

Most of the iron(II), hydrogen, and sulfate ions released during pyrite oxidation undergo various further reactions in the soil. Essentially all Fe(II) is further oxidized to Fe(III) in oxides, in the basic sulfate jarosite and in clay minerals. Most of the sulfate remains in solution and is removed by leaching, together with cations (mainly Mg, Ca and
Na) derived from ion exchange and mineral weathering. The remainder of the sulfate is precipitated as jarosite and as basic aluminum sulfate, and part is adsorbed, especially at low pH. Gypsum and other more readily soluble sulfates may form, often temporarily, when evaporation exceeds rainfall.

**Jarosite.** The predominant Fe sulfate mineral in acid sulfate soils is the sparingly soluble jarosite \([\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6]\). It commonly occurs as earthy fillings of voids or as mottles in the soil matrix, and gives a sharp X-ray diffraction pattern. Jarosite is a member of the alunite group, a series of basic sulfates with the general formula \(\text{AB}_3(\text{SO}_4)_2(\text{OH})_6\) in which A stands for \(\text{K}^+, \text{Na}^+, \text{H}_3\text{O}^+, \text{or NH}_4^+\), and B for Fe(III) (jarosite) or Al (alunite). A virtually complete solid solution exists between jarosite (the K form), natrojarosite, and hydronium jarosite, but K-form is the most common in coastal acid sulfate soils. The theoretical pe-pH stability diagram indicates that jarosite is formed only in acid (pH 2 - 4), oxidized (Eh > 400 mV) environments (Ivarson et al., 1982). The pale yellow (2.5 - 5Y 8/3 - 8/6) mottles are so characteristic that they are used, together with pH, as a diagnostic criterion for classifying acid sulfate soils. On the other hand, jarosite is lacking in some acid sulfate soils, particularly those high in organic matter (Kosaka, 1971).

**Iron oxides.** Eventually most of the iron from oxidized pyrite ends up in Fe(III) oxides. Fine-grained goethite may
form either directly, and quickly, upon oxidation of dissolved Fe(II) sulfate released during pyrite oxidation, or more slowly, by hydrolysis of jarosite. Both reactions are acidic and part of the sulfuricization process:

$$\text{Fe}^{2+} + 2\text{SO}_4^{2-} + \frac{1}{4}\text{O}_2 + 3/2\text{H}_2\text{O} \rightarrow \text{FeOOH} + 2\text{H}^+ + \text{SO}_4^{2-} \quad [4]$$

$$\text{jarosite} \rightarrow 3\text{FeOOH} + 2\text{SO}_4^{2-} + \text{K}^+ + 3\text{H}^+ \quad [5]$$

At pH values below 6, Fe(III) oxides are incompatible with pyrite, and indeed, most of the iron oxide is formed at an appreciable distance from pyrite. By contrast, at high pH, as in calcareous pyritic sediments, goethite is often pseudomorphic after pyrite.

In the better drained, deeply developed acid sulfate soils, part of the Fe(III) oxides in the B horizon may occur as hematite, giving conspicuous red mottles. In Thailand, these red mottles are unknown from non-acid marine soils, and they are used as a field indicator of moderately to strongly acidic conditions (van der Kevie and Yenmanas, 1972).

**Basic aluminum sulfates.** The soil solution of acid sulfate soils is generally supersaturated with alunite, the aluminous counterpart of jarosite (van Breemen, 1973). The activity of dissolved Al in acid sulfate soils in the field, as well as in more oxidized pyritic soil in the laboratory, seems to be regulated by jurbanite [AlOHSO$_4$] (van Breemen, 1973; 1982).

**Water soluble sulfates.** Gypsum has been observed in coastal marine soils over a wide pH range (3.5 - 7.0). Due to its fairly high solubility, gypsum is confined to dryer soils or
to those containing calcium carbonate. Under arid conditions most soluble sulfate such as Na-alum, tamarugite [NaAl(SO₄)₂(H₂O)₆], pickeringite [MgAl₂(SO₄)₄(H₂O)₂₂] and rozenite [FeSO₄(H₂O)₂], can be formed, particularly on the surface of young acid sulfate soils or of excavated pyritic soil, where pyrite oxidation is relatively rapid (van Breemen, 1976). Precipitates of malaniterite [FeSO₄(H₂O)₇] and copiapite [Fe(II)Fe(III)₄(SO₄)₆(OH)₂(H₂O)₂₀] and coquimbite [Fe₂(SO₄)₃(H₂O)₉] have been found in association with acid mine drainage (van Breemen, 1988).

5.1.3 Solution chemistry of iron in acid soils

The concentration of Fe³⁺ in aqueous solution in equilibrium with ferric oxides is controlled by pH, whereas that of Fe²⁺ is controlled by a combination of pH and pe (16.9xEh). The solubility characteristics of the two species will be considered separately.

5.1.3.1 Ferric species

The measured activity of Fe³⁺ in well-aerated soil suspension (Norvell and Lindsay, 1982) is 500 times higher than that generated by goethite (α-FeOOH), the most stable of the ferric oxyhydroxides in water, and about 13 times higher than that generated by lepidocrocite (γ-FeOOH). Norvell and Lindsay termed the solid phase responsible "soil-Fe", which might correspond to ferrihydrite. In acid soils, ferrihydrite readily transforms to goethite or hematite, but its total Fe(III) concentration (consisting of Fe³⁺ + Fe(OH)²⁺ + Fe(OH)₃⁺)
+ Fe(OH)$_3$) is extremely low, falling below $10^{-6}$ M at around pH 3.4. Thus, acidity alone can mobilize little Fe(III).

The presence of complexing agents can increase significantly the amounts of Fe(III) in equilibrium solutions; e.g., oxalate, which is a strong complexing agent for Fe(III), at $10^{-4}$ M can maintain the concentration of total soluble Fe(III) above $10^{-5}$ M at pH 4.4 in the presence of soil-Fe. Although lower concentrations ($< 10^{-5}$ M) of oxalate are less effective, it is possible that local concentrations of microbially generated oxalate could be effective in the mobilization of iron in acidic surface horizons (Jones and Wilson, 1985).

5.1.3.2 Ferrous species

The concentration of Fe(II) in equilibrium with soil-Fe is described in the equation

$$\text{Fe(OH)}_3(\text{soil}) + 3\text{H}^+ + e^- \rightarrow \text{Fe}^{2+} + 3\text{H}_2\text{O},$$

for which the relationships

$$\log (\text{Fe}^{2+}) = 15.47 - (\text{pe} + \text{pH}) - 2\text{pH}$$

has been derived (Lindsay, 1979). The term (pe + pH) is constant for a constant partial pressure of O$_2$, or H$_2$, and ranges from about 17 on well-aerated soils to 3 in strongly reducing soils. It follows from this relationship that, in acid soils of pH 3 - 4, the activity of Fe(II) exceeds that of Fe(III) species in non-complexing solutions for values of pe + pH below 15 (Lindsay and Schwab, 1982).
In soils subjected to periodic waterlogging, redox processes assume prime importance in determining the chemistry of iron. In paddy fields, large fractions of the iron present as free Fe(III) oxides in aerated conditions become reduced to Fe(II) after comparatively short periods (a few months) of waterlogging (van Breemen, 1988). In most instances only a small fraction of the Fe(II) remains in solution, most of it ending up either in exchanged forms or as in sulfide minerals, such as mackinawite or pyrite (FeS₂).

5.2 Aluminum chemistry in acid soils

Several recent reviews of Al chemistry discuss the important forms and transformations of Al in details (Thomas, 1988; Paterson et al., 1991). Aluminum exists in numerous forms in both the solid and the liquid phases of soil. The forms of Al in the liquid phase (i.e. soil solution) are governed by hydrolysis, complexation and polymerization. Hence, the level of Al in soil solution will depend on the soil pH, amount and type of primary and secondary Al-containing minerals, exchange equilibria with inorganic surfaces and complexation with organic constituents (Bell and Edwards, 1986).

5.2.1 Hydrolytic reactions of Al

Aluminum has a high ionic charge, and a small crystalline radius (0.054 nm). Thus, it is very reactive in soil solution. When an Al-containing mineral dissolves, the released Al³⁺
coordinates with six OH₂ groups and forms an octahedral hydration sphere \( \text{Al(H₂O)₆}^{3⁺} \). As pH increases, each OH₂ group sequentially dissociates a H⁺ to produce the mononuclear hydrolysis products of \( \text{Al}^{3⁺} \), \( \text{Al(OH)}^{2⁺} \), \( \text{Al(OH)}⁺ \), \( \text{Al(OH)}₃⁻ \), and \( \text{Al(OH)}₄⁻ \) (coordinated OH₂ groups have been deleted for clarity) over the pH range of soils (Martin, 1988). This simple monomeric hydrolysis provides a satisfactory description of the pH and the Al⁺³ activity in dilute aqueous solutions at low basicities.

At high basicities or elevated OH:Al ratio in solution, polynuclear hydroxy-Al species, which are metastable intermediates in the precipitation of solid phase Al(OH)₃, may form (Driscoll and Schecher, 1988; Nordstrom and May, 1989). Various inorganic ligands including fluoride (F) and sulfate \( (\text{SO}_₄⁻) \) and a wide variety of organic ligands form soluble complexes with Al.

### 5.2.2 Solubility and precipitation of Al

Various solid phases have been implicated in the control of Al solubility in acid soils. Richburg and Adams (1970) suggested that gibbsite or gibbsite-like mineral controls Al solubility. Marion et al. (1974) concluded that gibbsite, halloysite, kaolinite or montmorillonite may govern Al solubility, depending on the soil. van Breemen (1973) suggested that basic aluminum sulfates may control Al solubility in acid sulfate soils. This hypothesis was supported by Nordstrom (1982), who claimed that \( \text{KAl}_3(\text{SO}_₄)_₂(\text{OH})₆ \).
(alunite), and Al₄(OH)₁₀SO₄ (basaluminite) likely controls Al solubility under acidic conditions if SO₄²⁻ activities are high enough.

Under some circumstances, the solubility equilibria cannot be used readily to predict Al concentration in acid soils for three reasons. (1) Soils generally do not contain thermodynamically pure solid phases and therefore cannot reach true equilibria (Helmke, 1988). (2) The kinetics of Al dissolution, polymerization, and precipitation reactions are so slow compared to changes in dissolved forms and activities from leaching and changes in soil water content that equilibrium is not likely to be approached (Baham, 1984; Goenaga and Williams, 1988). (3) Aluminum solubility, when expressed on a concentration basis, is generally increased by the presence of strong ligands (Burrows, 1977). Organic acids inhibit hydrolysis and precipitation of Al, perhaps by disrupting hydroxyl bridging (Kwong and Huang, 1979), and accelerates the dissolution of Al-bearing minerals (McColl and Pohlman, 1986). Huang (1988) reviewed the effects of soil solution ligands on the solubility and precipitation products of Al.

5.2.3 Aluminum speciation as an index of phytotoxicity

The relative phytotoxicity of mononuclear and polynuclear Al species have been assessed in short-term solution culture studies (Hue et al., 1986; Parker et al., 1988; Parker et al., 1989). These studies established the nontoxicity of Al-SO₄.
(Kinraide and Parker, 1987a), Al-F (Cameron et al., 1986) and organic complexes of Al (Hue et al., 1986). One polynuclear hydroxy Al species (Al\(_{13}\)) proved to be quite toxic in artificial solutions (Parker et al., 1989), but its role in soil Al toxicity is uncertain given the high affinity of negatively charged soil surfaces for Al polymers (Zelazny and Jardine, 1989). While Al\(^{3+}\) is generally considered to be the main toxic mononuclear species, the toxicity of Al(OH)\(^{2-}\) and Al(OH)\(_2\)\(^{+}\) has been claimed (Alva et al., 1986). Some investigators use the summation of the activities of these three mononuclear Al species as a measure of toxicity (Bell and Edwards, 1986). In recent studies wheat (monocotyledon) was shown to be sensitive to Al\(^{3+}\) but not to Al(OH)\(^{2-}\) and Al(OH)\(_2\)\(^{+}\) (Kinraide and Parker, 1989a). Dicotyledonous species, however, appeared to be sensitive to mononuclear hydroxy-Al and unaffected by Al\(^{3+}\) (Kinraide and Parker, 1989b). The authors suggest that determining the relative toxicities of Al\(^{3+}\) and mononuclear hydroxy-Al may be an intractable problem because the hydroxy-Al monomers can be expressed as a function of the activities of Al\(^{3+}\) and H\(^+\). Therefore, toxicity attributed to mononuclear hydroxy-Al may be Al\(^{3+}\) toxicity influenced by pH (Kinraide and Parker, 1989b).

Plant growth limitations have generally been expressed as a function of activity of Al\(^{3+}\) [(Al\(^{3+}\)]. A plot of relative taproot length of soybean (Glycine max (L.) Merr.) versus calculated (Al\(^{3+}\)) is reported by Noble et al. (1988). This
graph illustrates the sensitivity of root elongation to (Al$^{3+}$) in a complete nutrient solution and is typical of the response pattern to Al stress exhibited by a number of plant species. Treatments that reduce (Al$^{3+}$), including increasing the pH of the system and the addition of Al complexing ligands, have been shown to ameliorate Al toxicity (Parker et al., 1988). Lime addition is often used to overcome soil acidity but materials containing Al complexing ligands (SO$_4^-$, F) have also been used (Sumner and Carter, 1988). Calcium and other cations have been shown to reduce Al toxicity in solution culture experiments (Kinraide and Parker, 1987b). These salt additions increase ionic strength and hence reduce (Al$^{3+}$). The cations also have a direct physiological effect on the plants, perhaps by competing with Al$^{3+}$ for external binding sites on root cells. In general, some function of solution (Al$^{3+}$) and (Ca$^{2+}$) gives a better prediction of root growth than (Al$^{3+}$) alone (Noble and Sumner, 1988).

5.3 Al detoxification by organic amendments

Polyvalent aluminum ions are bound reversibly on cation exchange sites, and almost irreversibly by ligand bonds, to organic surfaces (Hargrove and Thomas, 1981a). Addition of organic amendments (crop residues, animal waste, and green manure) appears to provide alternative adsorption sites for Al$^{3+}$. 
5.3.1 Influences of plant residues, sewage sludge and animal wastes

In fact, several studies have demonstrated a considerable reduction in soluble and exchangeable Al concentration by organic matter applications to very acid soils (Brogan, 1967; Hoyt and Turner, 1975). The incorporation of crop residues, such as ground coffee (*Coffea sp*) leaves and pangola grass (*Digitaria decumbens* Sent) into a strongly acid soil of Puerto Rico significantly reduced both exchangeable and soil solution Al, and enhanced growth of sorghum (Wahab and Lugolopez, 1980). It has been observed that plant residues like alfalfa (*Medicago sativa*) meal (Hoyt and Turner, 1975), wheat (*Triticum aestivum*) straw (Ahmad and Tan, 1986), green manure leaves of cowpea (*Vigna unguiculata*) and leucaena (*Leucaena leucocephala*), and pineapple (*Ananus comosus*) leaves (Hue and Amien, 1989; Lu, 1991) added to Al-toxic soils reduced the toxicity of Al and increased the biomass production of plants grown in those soils. Similarly, the critical Al concentration above which Al phytotoxicity occurs, increases with increasing the content of soil organic matter (Adams and Hathcock, 1984).

Sewage sludge and animal wastes, such as poultry and cattle manures, have also been reported to reduce Al toxicity and increase rice (*Oryza sativa*) yields (Ragland and Boonpuckdee, 1986), and forage yield of *Desmodium intortum* (Hue, 1992). In particular, chicken manure is known to contain significant
amounts of uric acid in addition to many other organic molecules (Tan et al., 1971; Hue, 1992). The structure of uric acid is a heterocyclic molecule with chemical structure similar to that of 8-hydroxy quinoline in terms of forming a 5-membered ring with Al. Since the latter compound is a strong Al complexer as indicated by its use in the colorimetric determinations of Al (Bloom et al., 1978), uric acid and its supply source (chicken manure) is expected to strongly complex Al.

5.3.2 Al detoxification by organic complexation

Al ions are detoxified by interaction with organic matter and its decomposition by-products through complexation, chelation and peptization (Bartlett and Riego, 1972; Cabrera and Talibudeen, 1977; Hue et al., 1986). Organically complexed Al would not be absorbed by roots or may be taken up by plants without the adverse effects on growth and yields.

Low-molecular-weight organic acids have been shown to reduce Al phytotoxicity without reducing its total concentrations (Bartlett and Riego, 1972). By using the elongation rate of cotton (Gossypium hirsutum L.) taproots as a bioassay index of Al toxicity, Hue et al. (1986) measured the relative toxicity of Al in the presence of several naturally occurring organic acids in acid forest soils. The detoxifying capabilities of these acids appear to increase with concentration and the proximity of hydroxyl and carboxylic groups within the molecule, and follow the order
citric > oxalic > tartaric > malonic > salicylic. This suggests that complexation involving Al, hydroxyl and carboxyl groups, resulting in stable 5- or 6-membered ring structures, was primarily responsible for the Al detoxification. Humic acids reduced the toxicity of Al by reducing the concentration of Al in soil solution and the quantity of KCl-extractable Al (Bloom et al., 1979; Hargrove and Thomas, 1981b). Addition of 100 and 350 µg g⁻¹ humic acid to maize in sand culture increased yields and reduced leaf Al concentration from 86.6 µg g⁻¹ to 57.4 µg g⁻¹ (Tan and Binger, 1986). Soluble organic ligands can reduce the toxicity of Al without necessarily reducing the soil solution concentration or plant uptake. Citric acid, which occurs at 10⁻⁶ - 10⁻⁵ M concentrations in soil solution, increased translocation of Al to the tops of ryegrass (*Lolium multiflorum* Lam) with no apparent effect on dry matter yield (Muchovej et al. 1986).

In addition to transforming soluble Al from phytotoxic to nontoxic forms without changing the soluble Al concentrations, the added organic materials could also precipitated Al by increasing the soil solution pH as a result of intense microbial activities or of ligand exchange between organic anion and terminal OH⁻ of the variable-charge soils (Parfitt et al., 1977b; Hue and Amien, 1989). Consequently, exchangeable Al⁺³ as extracted with unbuffered 1 M KCl can also be reduced by the addition of organic matter (Evans and Kamprath, 1970; Hansen et al., 1988). Chelation of Al⁺³ by
different functional groups (-OH, -COOH and -NH₂) of the solid portion of organic matter could also play an important role in reducing exchangeable Al (Hoyt and Turner, 1975; Hargrove and Thomas, 1981a).

5.4 Green manures and organic management for acid soils

Past research has concentrated on green manure application to lowlands to improve rice yield (Naklang et al., 1980a, 1980b). The results often suggest that the incorporation of sunn hemp markedly increased the growth and yield of rice, especially when sunn hemp residue was used continuously and/or combination with chemical fertilizer.

For upland acid soils under field crops, some experimental results have been encouraging. Effect of green manure on sorghum yield has been reported by Thawornmas and Dechsongchan (1979). It was found that the incorporation of Vigna spp and Crotalaria juncea increased the yield of sorghum by 2350 and 3437 kg ha⁻¹, respectively. Also, long term rotations of green manure-corn were practiced for six years at the National Corn and Sorghum Research Center in Nakhon Ratchasima. The experiment plots were on a Pak Chong soil (Kandiustults, pH 5.2). It was observed that the yields of corn improved under repeated rotation of Mimosa invisa and Sesbania speciosa, and reached a plateau of 6 - 7 tons ha⁻¹ in the fourth rotation. Treatments of N and NP fertilizer accelerated the rate of yield improvement to a certain extent but did not show any
distinct advantage after the fourth rotation. Soil analyses clearly showed an accumulation of total N (2.12%) and organic matter (1.8%) under both mimosa and sesbania rotations, indicating an abundant supply of organic N from the legumes (Sukthumrong et al., 1986).

In Thailand, the use of organic industrial wastes as a source of nutrients for paddy rice has been of considerable interest in recent years (Vacharotayan and Yoshida, 1985; Vacharotayan et al., 1988). Cooperative work between Thailand and Japan has indicated that organic industrial wastes, especially castor meal and activated sludges, could be effectively used as source of nitrogen for paddy rice and upland crops (Panichsakpatana et al., 1988). The efficiency of glutamic mother liquor (GML) and 'humus', the organic waste materials from a monosodium glutamate factory, as a source of N for paddy in acid sulfate soils (Rangsit series; Sulfic Tropaquepts) was evaluated in the laboratory and pot experiments (Chanchareonsook et al., 1989). It was found that grain yield of the rice plants grown in the soil amended with GML was 83 and 82% of those grown in the soil amended with \((\text{NH}_4)_2\text{SO}_4\) and urea, respectively. 'Humus' increased both the growth and yield of rice but the effectiveness was very low as compared to GML. The low efficiency of 'humus' might be due to the effects of some toxic substances released from decomposition which reduced the number of grain sets per panicle.
Some organic wastes have been shown to reduce the adverse effects of acidity in some soils from the Northeast Thailand. Ratanarat et al. (1977) showed that the application of lime together with organic compost resulted in the highest yield of soybean grown on acid Roi-et soil (Aeric Paleaquult, pH 4.8 and 0.9% O.M.). Lower tissue concentrations of Al and Mn in the plants treated with lime-compost were probably responsible for such a superior growth.

5.5 Influence of soil organic materials on aluminum transformation

5.5.1 Formation of soluble organic-aluminum complexes

5.5.1.1 Formation and stability of bonds

Aluminum may form soluble or insoluble complexes with organic matter or it may be non-specifically adsorbed onto exchange sites. Evidence for insoluble organic Al complexes comes from studies using infra-red spectroscopy. Vinkler et al. (1976) considered that the antisymmetric carboxylate stretching frequency at 1625 - 1630 cm\(^{-1}\) for Al humates and fulvates indicated the formation of covalent rather than ionic bonds. By bonding with various functional groups of a humic acid, Ritchie et al. (1982) demonstrated that carboxyl and phenolic OH-groups were responsible for formation of complexes with Al\(^{3+}\), Fe\(^{3+}\) and Cu\(^{2+}\). The high pH at which phenolic hydroxyls deprotonate prevent them from binding Al\(^{3+}\) in acid solution. If Al binds to a carboxyl adjacent to phenolic OH,
however, the OH is more easily deprotonated, and may form part of bidentate chelate ring (Lind and Hem, 1975). Aluminum also forms chelates with adjacent carboxyl groups on ligands. Complexes of Al and organic ligands have been reported as Al-oxalate (oxalate forming a 5 member ring), Al-tartrate 2 (2 tartrate ligands forming 7 member ring), and Al-citrate (citrate forming 3 rings with 7, 6, and 5 members) (Motekaitis and Martell, 1984).

Factors which influence the stability of Al-organic complexes include the number of ligand atoms bonded to the metal atom, the number and arrangement of rings formed, and the presence of competing cations and ligands, especially H\(^+\) and OH\(^-\) (Stevenson, 1982). Formation of stable chelates requires that reactive functional groups are in close enough to form rings with the central metal atom. Therefore, the stability of Al complexes with humified polymers is inversely related to the distance between carboxyl groups (Arai and Kumada, 1981).

### 5.5.1.2 Solubility of organic-Al complexes

Low molecular weight organic ligands are capable of forming soluble complexes with Al (Motekaitis and Martell, 1984; Hue et al., 1986). Complexation with Al can cause larger fulvic acid molecules to precipitate out of solution (Schnitzer, 1978).

Aluminum forms insoluble complexes with insoluble humified organic matter. The formation of complexes with
insoluble organic polymers can also be described as adsorption. Increasing soil organic matter content may result in decreasing soil solution and KCl-extractable Al (Thomas, 1975).

5.5.1.3 Significant role of pH

Organic-aluminum complexation is pH dependent. The addition of organic matter to a soil or solution can decrease or increase the level of soluble Al depending on the concomitant changes in pH (Bloom et al., 1979). Increases in soluble Al could be explained by the high pH of the soil causing some dissociation of $H^+$ from the organic matter which lowered the soil pH and resulted in the dissolution or release of Al. On the other hand, the addition of organic matter could also decrease soluble Al because the extent of Al binding by the organic matter more than counterbalances any increased Al dissolution caused by pH decreases (Hargrove and Thomas, 1981b). Hargrove and Thomas (1982) observed a pH increase with Al adsorption when the soluble Al was present mainly as hydrolyzed species initially. This reaction was probably due to the low pH of the organic matter suspension partially dehydroxylating some of the added Al. In contrast, Arai and Kumada (1981) and Hargrove and Thomas (1982) observed a pH decrease when Al was adsorbed by organic matter from solution at pH < 4. In the latter cases, the Al would have been present primarily as Al$^{3+}$ and its adsorption could have involved
exchange with H\(^+\) ions as well as some surface hydrolysis. Both mechanisms would decrease pH.

5.5.2 Adsorption of organic anions on variable-charged surfaces of aluminum, and iron minerals

Organic anions which form complexes with dissolved aluminum and iron can also be specifically adsorbed on variable-charge surfaces of Al and Fe clays and hydrous oxides. Specific adsorption denotes adsorption through other than electrostatic binding (Stumm et al., 1980). In ligand exchange, one or more reactive groups form an inner-sphere complex with Al or Fe on hydroxylated mineral surfaces, displacing surface hydroxyls (Sposito, 1984). The surface hydroxyls are amphoteric, and may be protonated (-OH\(_2\)) or deprotonated (-O\_), depending on pH. Ulrich and Sumner (1991) illustrate possible results of the specific adsorption of a di- and tricarboxylate anion on a variable-charge Al mineral with varying degrees of protonation.

5.5.2.1 Evidence for ligand exchange

Several authors present evidence that organic anions are specifically adsorbed on mineral surfaces through ligand exchange with carboxylate and surface hydroxyls. Stumm et al. (1980) inferred the formation of inner-sphere complexes of various ligands with goethite and gibbsite from the similarity of stability constants of those complexes with analogous complexes with soluble iron and aluminum. The decrease in organic anion adsorption as pH increased above the pKa of the
carboxyl, reported by several authors (Bowden et al., 1980; Kummert and Stumm, 1980), has been suggested as evidence for a ligand exchange reaction analogous to the formation of solution complexes.

Parfitt et al. (1977a) measured adsorption of oxalate and benzoate on gibbsite and goethite. The adsorption of oxalate was consistently greater than benzoate under identical conditions. By comparing the infrared spectra of the surface complexes with model compounds and complexes, the authors concluded the following. At low concentrations of 100 μmol g⁻¹, oxalate was adsorbed on goethite as a binuclear complex across adjacent Fe atoms. At higher concentrations a monodentate complex formed. Oxalate formed a bidentate complex with single atom of Al on gibbsite edges. Oxalate and benzoate did not adsorb onto faces of the gibbsite used in the study. At pH 3.5 fulvate was adsorbed onto the gibbsite faces, perhaps by hydrogen bonding. The authors suggested that poorly crystalline hydrous Al oxides would contain more sites for ligand exchange than the gibbsite used in their study (Parfitt et al., 1977b).

Huang et al. (1977) confirmed the importance of amorphous hydrous oxides in organic anion adsorption. Dissolution of amorphous hydrous oxides from four Taiwan soils reduced adsorption of five aromatic carboxylic acids. One of the soils (an Alfisol) was coated with hydroxy-Al and -Fe
precipitates. The hydroxides coatings increased adsorption of all of the aromatic acids studied.

Specific adsorption of organic anions alters soil properties in three ways which may benefit plant growth. (1) Specific adsorption can potentially raise soil pH by displacing surface hydroxyls into the soil solution, and precipitate Al. (2) Specific adsorption of organic anions may increase cation nutrient retention by increasing negative charge on hydrated oxide or clay surfaces. (3) At low pH, adsorption of organic anions may enhance the availability of nutrient oxyanions, such as phosphate, by competing for adsorption sites and by reducing positive charge.

5.5.2.2 Effects of adsorption on soil pH

Parfitt et al. (1977b) measured OH- release during adsorption of oxalate by gibbsite, and fulvate by gibbsite and goethite (Parfitt et al., 1977c) by back-titrating suspensions to their original pH after organic anion additions. The first 25 μmol g⁻¹ oxalate released approximately 1.3 moles of OH- per mole of oxalate adsorbed. Adsorption of 50 g kg⁻¹ fulvate released approximately 10 cmol (OH) kg⁻¹ from goethite and 20 g kg⁻¹ released approximately 2.5 cmol (OH) kg⁻¹ from gibbsite.

A few report of increases in soil pH with additions of organic material can be found in the literature. After 14 days of incubation, coffee (Coffea arabica L.) leaves raised the pH of a Puerto Rican Typic Humult (Wahab and Lugo-Lopez, 1980). Lopez-Hernandez et al. (1986) reported a pH increase in soil
suspensions after malate was added. After ground alfalfa (Medicago sativa L.) hay was incorporated into a Canadian soil, pH increased for 6 weeks and remained nearly constant for an additional 14 weeks before decreasing (Hoyt and Turner, 1975). An excess of pH 6.1 fulvate added to suspensions of gibbsite or goethite at pH 6.3 raised pH over 2 units (Parfitt et al., 1977c). Sodium humate also raised pH of suspensions of the same minerals. Incorporation of 8 Mg ha⁻¹ fresh weight of Kudzu (Pueraria Phaseoloides) tops in a Peruvian Ultisol increased soil pH with a corresponding reduction of KCl-extractable Al and Al saturation relative to an unamended treatment (Wade and Sanchez, 1983). The difference between the green manure and control was greatest 15 months after incorporation.

Asghar and Kanehiro (1980) incubated large quantities (5 and 10% of soil mass) of sugarcane (Saccharum officinarum) and pineapple (Ananas comosus) residue in a Rhodic Eutrustox. Each treatment resulted in an initial increase in soil pH. The pH of the pineapple amended soil remained higher than the unamended throughout the experiment (120 days). The increase and subsequent decrease of pH was linearly related (r² = 0.71, p < 0.01) to changes in Eh measured with a platinum electrode. The authors attributed the changes in soil pH to the redox reaction,

\[ \text{MnO}_2 + 2H^+ + 2e^- \rightarrow \text{Mn}^{2+} + 2OH^- \] [7]
with the availability of e\textsuperscript{-} positively related to microbial activity.

### 5.5.2.3 Effects of adsorption on surface charge

Adsorption of organic anions may improve the retention of nutrient cations. By reducing the number of protonated sites on a hydrous oxide surface, adsorption of organic anions tends to reduce surface positive charge over a range of pH, and reduce the zero point of net charge of the oxide (Kummert and Stumm, 1980). Plant materials (*Canavalia ensiformis* and *Panicum maximum*) incorporated into a Brazilian Typic Haplustox increased negative charge of the soil (Motavalli et al., 1988).
References


Bowden, J.W., S. Nagarajah, N.J. Barrow, A.M. Posner, and J.P. Quirk. 1980. Describing the adsorption of phosphate,


region as affected by organic waste materials with the reference of NRCT-JSPS cooperative research in Thailand. 240 p.


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CHAPTER 6

Selected physical and chemical properties of acid sulfate soils used in the present study

6.1 General description of the soils

Two acid sulfate soils from the Bangkok Plain, Thailand were used in this dissertation. They are Rangsit very acid phase series (Ra), and Bang Pakong series (Bg), and are hydromorphic alluvium. Details of site selection, morphology and profile description are listed in Appendix A-1 and A-2.

The Ra soil (Sulfic Tropaquepts), an extremely acid soil, represents the suitability class P-IVa (in Thailand). Soils in this class have severe limitations due to acidity constraints that restrict their use for rice production and/or require very special management.

The Bg soil (Typic Sulfaquents) represents potential acid sulfate soils. Its suitability classification for rice production is dependent on the level of salinity and the degree of oxidation of the surface soil. The soil will turn into class P-IVa after intense oxidation.

6.2 Site selection and soil sample preparation

Figure 6.1 shows the locations where the two acid sulfate soils were collected. The Ra soil was sampled from two local farms and the Ongkarak Acid Sulfate Soil Experiment Station in the Nakhon Nayok Province. The Bg soil was located about 45 km
**Figure 6.1.** Generalized soil map of the Southern Bangkok Plain (after Province Series No. 8, Dept. of Land Development, Bangkok. 1972) showing the sampling site as: II. Rangsit very acid phase, at Nakhon Nayok Province; and IV. Bang Pakong, at Chachoengsao Province.

east of the Ra soil. The Bg soil was collected from two local farms and the Bang Pakong Soil Conservation Center in the
Chachoengsao Province. The soil samples were collected in the early rainy season (August, 1992). Approximately 800 kg of a composite sample from each soil series was collected from the plow layer (20 cm) and the jarositic horizon (30 - 60 cm) in a half hectare area. The samples were transported to the Department of Soil Science, King Mongkut's Institute of Technology, Ladkrabang, Bangkok, where the soils were spread on large floors and allowed to air dry for 2 - 3 weeks. Finally, the soils were ground with a mechanical grinder and sieved to pass a 2-mm screen before use. About 20 kg of each soil was shipped to the University of Hawaii for an incubation study.

6.3 Chemical characteristics of the aerated soils

Composite samples were used for each analysis. The parameters analyzed, methods and instruments used are as follows.

The pH and electrical conductivity (EC) in water (1:1) were determined by a pH meter equipped with a combination glass-calomel electrode, and conductivity meter as described by Attanandana and Chancharoensook (1980).

Organic matter was analyzed by the Walkley-Black method (Black, 1965). Total nitrogen was determined by the Kjeldahl method (Bremner, 1965). Extractable P was determined by the Bray II method (Bray and Kurtz, 1945).
Cation exchange capacity (CEC) was determined using ammonium saturation-distillation method as described by Chapman (1965).

Exchangeable K, Ca, Mg and Na - the soils were extracted with 1 M NH₄OAc (pH 7.0) as described by Black (1965). Potassium, Ca, Mg, and Na in the extract were determined by atomic absorption spectrophotometry. Total exchangeable base was the sum of exchangeable K, Na, Ca, and Mg.

Total exchange acidity, and exchangeable Al were extracted with 1 M KCl as described by Mclean (1965). Following extraction, a known aliquot was titrated. Exchangeable H was calculated as the difference between total exchange acidity and exchangeable Al.

For water soluble SO₄²⁻, the soils were extracted by the method described by Freeney (1986). Then, SO₄²⁻ ions were determined by the turbidimetric method.

For extractable Fe and Mn, the soils were extracted with 0.005 M DTPA, pH 7.30 as described by Lindsay and Norvell (1978).

Selected chemical properties of the two acid sulfate soils are listed in Table 6.1. The air-dried pH of both Bg and Ra soils was very low of 3.3 - 4.3 (average 3.8 for the Bg soil), and pH of 3.3 - 5.2 (average 4 for the Ra soil). The pH of the air-dried surface layers was usually above 4 because of high organic matter content.
Organic matter content in the Bg and Ra soils used in this study was higher than expected in as much as ranged from 2.9 - 5.5%, with the highest average value of 4.1% in the Bg surface soil. These values are probably due to slow decomposition of organic residues under strongly acid conditions.

In general, the extractable P in the Bg and Ra soils was insufficient for plant growth. The Bg soil had only 8.4 mg P kg⁻¹. Exchangeable K, Ca, Mg and base saturation in both soils

Table 6.1. Some important chemical properties of the aerated acid sulfate soils.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Soil Series</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bang Pakong (Bg)</td>
</tr>
<tr>
<td>pH (1:1; soil : water)</td>
<td>3.8</td>
</tr>
<tr>
<td>Organic matter (%)</td>
<td>4.15</td>
</tr>
<tr>
<td>Total N (%)</td>
<td>0.19</td>
</tr>
<tr>
<td>Extractable P (mg kg⁻¹)</td>
<td>8.40</td>
</tr>
<tr>
<td>CEC (cmol, kg⁻¹)</td>
<td>21.40</td>
</tr>
<tr>
<td>Total exchangeable base</td>
<td>11.28</td>
</tr>
<tr>
<td>(cmol, kg⁻¹)</td>
<td></td>
</tr>
<tr>
<td>Exchangeable K (cmol, kg⁻¹)</td>
<td>0.15</td>
</tr>
<tr>
<td>Exchangeable Ca (cmol, kg⁻¹)</td>
<td>2.20</td>
</tr>
<tr>
<td>Exchangeable Mg (cmol, kg⁻¹)</td>
<td>6.75</td>
</tr>
<tr>
<td>Exchangeable Na (cmol, kg⁻¹)</td>
<td>2.17</td>
</tr>
<tr>
<td>Exchange acidity (cmol, kg⁻¹)</td>
<td>14.36</td>
</tr>
<tr>
<td>Exchangeable Al (cmol, kg⁻¹)</td>
<td>7.56</td>
</tr>
<tr>
<td>Exchangeable H (cmol, kg⁻¹)</td>
<td>6.80</td>
</tr>
<tr>
<td>Extractable Fe (mg kg⁻¹)</td>
<td>1440.92</td>
</tr>
<tr>
<td>Extractable Mn (mg kg⁻¹)</td>
<td>36.80</td>
</tr>
<tr>
<td>Water soluble SO₄²⁻ (mgS kg⁻¹)</td>
<td>502.44</td>
</tr>
</tbody>
</table>
were low, whereas exchangeable Al was high. From the data presented, the Bg soil had 7.5 cmol$_e$ kg$^{-1}$ exchangeable Al, and the Ra soil, 4.3 cmol$_e$ Al kg$^{-1}$. Moreover, exchangeable H was high with contributing 40% of the total acidity.

The high proportion of exchangeable Mg to exchangeable Ca in the Bg soil is indicative of old marine sediments as the parent material. Extractable Fe, Mn and water soluble SO$_4^{2-}$ also differed markedly between the two soils, and they were much lower in the Ra soil. These inherent properties of two acid sulfate soils together with their relatively low pHS indicate a low fertility status and potential for the release of soluble Al and Fe in toxic amounts upon land use.

### 6.4 Particle size distribution

Particle size determination was carried out by the method of Gee and Bauder (1982). The percentages of clay, silt, and sand size fractions and the corresponding texture class are listed in Table 6.2. The two soils had clay textures, and the clay content ranged from 61.7% in the Ra soil to 55.7% in the Bg soil. A considerable vertical and lateral variation in soil texture however, may be found in field conditions, especially in smaller coastal plains, as near Bang Pakong. In the Bangkok Plain, textures are more uniform in the older acid sulfate soils (e.g., Ra, typically 60 - 65% clay in most soils) than in the zone closer to the coast, where soil with a silty clay texture (e.g., Bg) can be found.
Table 6.2. Particle size distribution and textures of the two acid sulfate soils.

<table>
<thead>
<tr>
<th>Soil Series</th>
<th>Clay (&lt; 2 μm)</th>
<th>Silt (50 - 2 μm)</th>
<th>Sand (&gt; 50 μm)</th>
<th>Texture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bg</td>
<td>55.76</td>
<td>39.76</td>
<td>1.04</td>
<td>Clay</td>
</tr>
<tr>
<td>Ra</td>
<td>61.71</td>
<td>35.63</td>
<td>2.63</td>
<td>Clay</td>
</tr>
</tbody>
</table>

6.5 Lime titration curves

According to Frink (1973), when an acid soil is neutralized, at least three reactions occur. First, exchangeable H is neutralized. Next, exchangeable and some parts of non-exchangeable Al are neutralized over a pronounced buffer range of 4.5 - 5.0. Finally, H bound at the edge sites of clay minerals and the weak acid groups of organic matter are neutralized, and the buffer range is above pH 5.5 - 6.0.

Figure 6.2 shows the lime titration curves of the two acid sulfate soils (using the methods described by Attanandana and Chancharoensook, 1980). By normal liming standards, these soils require enormous quantities of lime to raise soil pH by one unit. For example, 10 cmol (OH⁻) kg⁻¹ (or 10 ton CaCO₃ ha⁻¹) is needed to raise pH of the Ra soil from 4.0 to 5.0, and nearly 15 cmol (OH⁻) kg⁻¹ is required to raise pH of the Bg soil from 3.8 to 4.8. If pH 5.5, a traditionally recommended pH value, is attempted, then at least 13 and 21 ton CaCO₃ ha⁻¹ must be applied to the Ra and Bg soils, respectively.
Figure 6.2. Titration curves of the two acid sulfate soils. Bg = Bang Pakong, Typic SulfAquents; Ra = Rangsit, Sulfic Tropaquepts.
References


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CHAPTER 7

Differential acidity tolerance of tropical legumes grown for green manure in acid sulfate soils

7.1 Abstract

The growth and soil acidity tolerance of four tropical green manure legumes (Cajanus cajan, Sesbania aculeata, S. rostrata, and S. speciosa) were studied in a greenhouse experiment. Two acid sulfate soils (Typic Sulfaquents, Bg Series; and Sulfic Tropaquepts, Ra Series) were adjusted to four pH levels: 3.8 and 4.0 (original soil pH), 4.5, 5.5, and 6.5 (amended with lime). Plant dry weight was determined 49 days after sowing along with N, P, K, Ca, Mg, Fe, Mn, and Al concentrations in aerial plant parts.

The legumes responded differently to soil acidity and liming, but not to soil type. Cajanus cajan had the highest biomass production, followed by S. aculeata, S. rostrata and S. speciosa, in this order. Nitrogen content closely paralleled biomass production, suggesting that the symbiotic rhizobia and nodulation were perhaps more susceptible to soil acidity than the host plants. Liming to pH 5.5 was recommended for the legumes' growth based on sharper yield increases as soil pH was raised from 4.5 to 5.5 than from pH 5.5 to 6.5. In the unlimed soils, C. cajan and S. aculeata accumulated Ca concentration (0.32%) twice as much as the other two low-yielding legumes (0.15%). Furthermore, plant Ca increased
exponentially (or quadratically in the case of *S. speciosa*) as lime additions increased. It was estimated that *C. cajan* required approximately 1.2% Ca, *S. aculeata* 1.0%, *S. rostrata* 0.8%, and *S. speciosa* 0.5% for adequate growth. In contrast to the Ca accumulation pattern, Fe and to a lesser extent Mn were significantly lower in *C. cajan* and *S. aculeata* than in *S. rostrata* and *S. speciosa*. The ratio of Ca to Al in plant tops was used to characterize plant tolerance to soil acidity, and to quantify the critical Al concentration in the plants. It appears that growth ≥ 90% of the maximum is only attainable when Ca/Al is ≥ 150 for *C. cajan* and *S. speciosa*, ≥ 200 for *S. rostrata*, and ≥ 300 for *S. aculeata*. *Cajanus cajan* tolerated up to 80 mg Al kg⁻¹, whereas significant growth reduction occurred in the *Sesbania* species at levels > 30 mg Al kg⁻¹ in their tops.

7.2 Introduction

Use of fast growing legumes, such as *Cajanus cajan*, *Leucaena* and *Sesbania* species, as green manure has long been an important cultural practice of subsistence farmers in the tropics (Evans and Rotar, 1987; Yost and Evans, 1987). Little scientific information concerning edaphic adaptability of these multipurpose plants is available. Data from India, where most green manuring research has been done, indicate that these green-manure plants can grow well in calcareous or sodic soils, but their performance in acid soils has not been
vigorously tested (Evans et al., 1983; Mappaona and Yoshida, 1993). As for crop tolerance to soil acidity, C. cajan and S. rostrata were the only tropical legumes for which data were available (Joshua et al., 1989; Nakano et al., 1992). Cajanus cajan reportedly grew better than S. rostrata in acid soils (Nakano et al., 1992). Perhaps because of this tolerance, C. cajan has been recommended as a promising crop for the Northeast Thailand (Khon Kaen Province), where most soils are sandy and acid (Wallis et al., 1988). Recently, Thai farmers are growing legumes for green manure in annual crop rotation over an increasingly large area of clay-textured acid sulfate soils of the Bangkok Plain (Poolpipatana's personal observation). These soils are strongly acidic and potentially phytotoxic when aerated because of the oxidation of pyrite and jarosite minerals (Parkpian et al., 1991). Given these circumstances, characterizations of green-manure plants that are tolerant of soil acidity are urgently needed. Thus, the objective of this study was to evaluate the acidity tolerance of four leguminous species commonly used as green manure when grown on acid sulfate soils.

7.3 Materials and methods

7.3.1 Plant selection from a field survey

Initially a field survey was conducted to investigate the species by soil environment interaction for local tropical legumes in the Bangkok Plain. Studied plants were potential
green manure, leguminous species of *Cajanus*, *Crotalaria*, *Desmodium*, *Leucaena*, *Vigna*, and *Sesbania*. Each location was visited several times in order to question farmers on growth behavior, biomass production and ability to survive under adverse conditions. After evaluation, the four most promising species for green manure were selected for the greenhouse study. They were *Cajanus cajan*, *Sesbania aculeata* (also known as *S. bispinosa*), *S. rostrata*, and *S. speciosa*.

### 7.3.2 Soil sampling and analysis

Acid sulfate soils were taken from two locations where paddy rice and tropical fruits were grown. They were the Bang Pakong (Bg) and Rangsit very-acid phase (Ra) series. The Bg was characterized as a preoxidized potential acid sulfate soil (Typic Sulfaquents) and the Ra was an actual acid sulfate soil (Sulfic Tropaquepts).

Soil samples for the experiment were collected from Ap horizons and jarositic layers. The samples were air-dried, ground, sieved to pass a 2-mm screen and stored for chemical analysis. Selected chemical properties of the soils are given in Table 7.1.

Soil pH and electrical conductivity (EC) of 1:1 soil to water suspensions were measured after 1 h of intermittent shaking. CEC was determined by 1 M NH₄OAc, pH 7.0 (Chapman, 1965). Extractable P was determined by the Bray-II method (Bray and Kurtz, 1945). Ca and Mg from the NH₄OAc extract were
Table 7.1. Selected physical and chemical properties of the acid sulfate soils used in the greenhouse experiment.

<table>
<thead>
<tr>
<th>Soil properties</th>
<th>Soil Series</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bg</td>
</tr>
<tr>
<td>pH (1:1; soil : water)</td>
<td>3.8</td>
</tr>
<tr>
<td>EC (1:1; dS m⁻¹)</td>
<td>0.7</td>
</tr>
<tr>
<td>Organic carbon (%)</td>
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</tr>
<tr>
<td>Extractable P (mg kg⁻¹) &quot;u&quot;</td>
<td>8.4</td>
</tr>
<tr>
<td>CEC (cmolₑ kg⁻¹) &quot;u&quot;</td>
<td>21.4</td>
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<tr>
<td>Exchangeable K (cmolₑ kg⁻¹)</td>
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<td>Exchangeable Ca (cmolₑ kg⁻¹)</td>
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</tr>
<tr>
<td>Exchangeable Mg (cmolₑ kg⁻¹)</td>
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</tr>
<tr>
<td>Exchangeable Na (cmolₑ kg⁻¹)</td>
<td>2.1</td>
</tr>
<tr>
<td>Exchangeable acidity (cmolₑ kg⁻¹)</td>
<td>14.3</td>
</tr>
<tr>
<td>Extractable Al (cmolₑ kg⁻¹)</td>
<td>7.5</td>
</tr>
<tr>
<td>Al saturation, % of CEC</td>
<td>29.5</td>
</tr>
<tr>
<td>DTPA-Extractable Fe (mg kg⁻¹)</td>
<td>1440.9</td>
</tr>
<tr>
<td>DTPA-Extractable Mn (mg kg⁻¹)</td>
<td>36.8</td>
</tr>
<tr>
<td>Water soluble SO₄²⁻ (mgS kg⁻¹)</td>
<td>502.4</td>
</tr>
<tr>
<td>Particle size distribution</td>
<td></td>
</tr>
<tr>
<td>Silt (%)</td>
<td>40.8</td>
</tr>
<tr>
<td>Clay (%)</td>
<td>56.8</td>
</tr>
</tbody>
</table>

"u" Bray P-II method  
"u" 1M NH₄OAc, pH 7.0 method

determined by atomic absorption spectrophotometry, and K and Na by flame photometry. Al was extracted by 1 M KCl and determined colorimetrically (Barnhisel and Bertsch, 1982). Water-soluble sulfate-S was extracted by shaking 10 g soil with 50 mL water for 30 minutes, followed by 5 minutes
centrifugation at 2000 g (relative centrifugal force). The supernatant was filtered and measured turbidimetrically, using a spectrophotometer at 420 nm (Freeney, 1986). Soil texture was determined by the pipette method of Gee and Bauder (1982).

7.3.3 Pot experiment

The treatments consisted of factorial combinations of four legume species and four soil pH levels (unamended, 4.5, 5.5, 6.5). Thus, there were 16 treatments replicated three times in a randomized complete block design. The soil pH levels of 4.5, 5.5 and 6.5 were established by adding 10, 22, and 38 cmol (OH⁻) kg⁻¹ as Ca(OH)₂ to the Bg soil, and 5.5, 14 and 22 cmol (OH⁻) kg⁻¹ to the Ra soil. To ensure that plant growth was not limited by nutrient deficiencies, the following nutrient solution was applied (mg kg⁻¹ soil): Na₂MoO₄·2H₂O, 0.67; H₃BO₃, 0.83; CuSO₄·5H₂O, 5; ZnSO₄·7H₂O, 10; MnSO₄·H₂O, 15; and KH₂PO₄, 176. Nitrogen was applied only with a rate of 24 mg N kg⁻¹ as NH₄NO₃ at the beginning of the experiment to initiate growth. The P rate, based on a previous P response experiment, was selected to produce 90% of maximum growth and to minimize the ameliorating effects that higher rates of P could have on Al toxicity (Jugsujinda et al., 1978). The nutrients were mixed with the soils, then incubated for 14 days at field water holding capacity before planting.

Five seeds of each legume, inoculated with appropriate rhizobial strains, were planted in 15-cm diameter pots filled
with 2 kg of soil. After germination, seedlings were thinned to 2 plants per pot. The pots were watered daily with deionized water, initially to 80% field capacity, and later to field capacity as demand increased. The experiment was carried out in a greenhouse at King Mongkut's Institute of Technology, Bangkok, during September - November 1991. Day temperatures were about 30 - 35 °C and night temperatures 18 - 22 °C.

At 49 days after sowing, plants were removed from the pots and aerial biomass (dry weight of tops) was obtained from oven dried samples (70 - 80 °C for 48 h). A subsample from each replicate was digested in a 3:1 nitric : perchloric acid mixture and analyzed for K, Ca, Mg, Al, Fe, and Mn by atomic absorption spectrophotometry and P by the molybdate/ascorbic acid colorimetric method. Plant N was measured by the micro-Kjeldahl method.

Analysis of variance was used to test the effect of soil pH, soil type, and plant species on dry-matter weight and nutrient uptake of the legumes. The relationship between relative dry-matter yield and Ca/Al ratio of plant tissues was established by nonlinear regression analysis, using PLOTIT® software (Haslett, MI., USA) to derive critical Al concentrations.

7.4 Results and discussion

The two acid sulfate soils selected for this study had at least two nutritional problems for the growth of the green-
manure legumes: Al toxicity and Ca deficiency (Table 7.1). The data on extractable Mn and Fe also indicated the toxicity potential of these elements. The effect of soil type on growth parameters was however, statistically insignificant; thus, growth data from the two soils were combined for subsequent analysis and discussion.

7.4.1 Differential growth as measured by dry matter yield and N accumulation

The dry-matter weights of the legumes as affected by soil pH are listed in Table 7.2. Dry weight production was affected significantly (P < 0.01) by species, soil pH and species x pH interactions, but not by soil series. Soil series also had no significant effects on plant composition (statistical analysis not presented). For this reason, the plant dry weights from the two soils were combined for regression analysis (Table 7.3) (unlimed pH was designated as 3.9 which is the average of 3.8 and 4.0, actual pH of the 2 unamended soils). Among the four legumes, *S. speciosa* and *S. rostrata* had the lowest yields, whereas *C. Cajan* and *S. aculeata* grew much better throughout the pH range tested (Table 7.2). Since high biomass is an important factor in selecting legumes for green manuring, *C. cajan* and *S. aculeata* appear to be much better than *S. speciosa* and *S. rostrata* as green manures. Within species, growth improved considerably as pH increased (Table 7.2).
Table 7.2. Dry-matter yield of the four green manure legumes grown on two acid sulfate soils from Thailand, and the associated analysis of variance.

<table>
<thead>
<tr>
<th>Soil pH</th>
<th>C. cajan</th>
<th>S. aculeata</th>
<th>S. rostrata</th>
<th>S. speciosa</th>
</tr>
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<tbody>
<tr>
<td>3.8</td>
<td>1.64</td>
<td>1.56</td>
<td>1.27</td>
<td>0.93</td>
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<tr>
<td>4.5</td>
<td>3.48</td>
<td>2.61</td>
<td>2.40</td>
<td>1.95</td>
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<td>5.5</td>
<td>5.04</td>
<td>3.96</td>
<td>3.29</td>
<td>2.36</td>
</tr>
<tr>
<td>6.5</td>
<td>5.55</td>
<td>4.61</td>
<td>4.50</td>
<td>2.64</td>
</tr>
</tbody>
</table>

Rangsit very acid-phase soil (Sulfic Tropaquents)

<table>
<thead>
<tr>
<th>Soil pH</th>
<th>C. cajan</th>
<th>S. aculeata</th>
<th>S. rostrata</th>
<th>S. speciosa</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>1.97</td>
<td>1.86</td>
<td>1.70</td>
<td>1.17</td>
</tr>
<tr>
<td>4.5</td>
<td>5.16</td>
<td>2.77</td>
<td>2.31</td>
<td>2.32</td>
</tr>
<tr>
<td>5.5</td>
<td>6.76</td>
<td>4.55</td>
<td>4.17</td>
<td>3.54</td>
</tr>
<tr>
<td>6.5</td>
<td>6.58</td>
<td>4.76</td>
<td>4.18</td>
<td>3.00</td>
</tr>
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</table>

Analysis of Variance (ANOVA)

<table>
<thead>
<tr>
<th>Variance</th>
<th>df</th>
<th>MS</th>
<th>F-value</th>
<th>Significance</th>
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<tr>
<td>Block</td>
<td>2</td>
<td>0.36</td>
<td>1.05</td>
<td>NS</td>
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<tr>
<td>Treatment</td>
<td>31</td>
<td>7.57</td>
<td>22</td>
<td>**</td>
</tr>
<tr>
<td>Soil series</td>
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<td>9.2</td>
<td>27</td>
<td>NS</td>
</tr>
<tr>
<td>Soil pH</td>
<td>3</td>
<td>44.7</td>
<td>131</td>
<td>**</td>
</tr>
<tr>
<td>Legume (L)</td>
<td>3</td>
<td>21.8</td>
<td>64</td>
<td>**</td>
</tr>
<tr>
<td>S x pH</td>
<td>3</td>
<td>0.9</td>
<td>2.65</td>
<td>NS</td>
</tr>
<tr>
<td>S x L</td>
<td>3</td>
<td>1.8</td>
<td>5.3</td>
<td>NS</td>
</tr>
<tr>
<td>pH x L</td>
<td>9</td>
<td>1.6</td>
<td>4.7</td>
<td>**</td>
</tr>
<tr>
<td>S x pH x L</td>
<td>9</td>
<td>0.4</td>
<td>1.2</td>
<td>NS</td>
</tr>
<tr>
<td>Error</td>
<td>62</td>
<td>0.34</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* NS : non-significant at the 0.05 level; ** : significant at the 0.01 level.
Table 7.3. Regression equation of dry-matter weight (Y, in g pot⁻¹) against soil pH (X) and plant N concentration (N, in %). There were 24 observations for each legume.

<table>
<thead>
<tr>
<th>Regression equation</th>
<th>Coefficient of determination (r²)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cajanus cajan</strong></td>
<td></td>
</tr>
<tr>
<td>Y = -30.1 + 12.2X - 1.0 X²</td>
<td>0.72**</td>
</tr>
<tr>
<td>Y = -2.15 + 2.07N</td>
<td>0.59**</td>
</tr>
<tr>
<td><strong>Sesbania aculeata</strong></td>
<td></td>
</tr>
<tr>
<td>Y = -12.8 + 5.2X - 0.39X²</td>
<td>0.83**</td>
</tr>
<tr>
<td>Y = -0.59 + 1.22N</td>
<td>0.47**</td>
</tr>
<tr>
<td><strong>Sesbania rostrata</strong></td>
<td></td>
</tr>
<tr>
<td>Y = -9.7 + 3.9X - 0.27X²</td>
<td>0.83**</td>
</tr>
<tr>
<td>Y = -1.69 + 1.72N</td>
<td>0.52**</td>
</tr>
<tr>
<td><strong>Sesbania speciosa</strong></td>
<td></td>
</tr>
<tr>
<td>Y = -14.8 + 6.1X - 0.52X²</td>
<td>0.78**</td>
</tr>
<tr>
<td>Y = 0.21 + 0.92N</td>
<td>0.46**</td>
</tr>
</tbody>
</table>

** Significant at the 0.01 level.

Quadratic relationships between dry-matter yield and soil pH (Table 7.3) suggest that 95% of the maximum yield would be attained when soil pH is 5.5 for *C. cajan*, 5.9 for *S. aculeata*, 6.3 for *S. rostrata*, and 5.3 for *S. speciosa*.

Along with biomass, high total N accumulation (mostly from N fixation) is another desirable characteristic of legumes to be used as green manure. This N criterion clearly indicates that *C. cajan* and *S. aculeata* are better green manures than *S. speciosa* and *S. rostrata* (Fig. 7.1 A). In fact, *S. speciosa* grew slowly, produced the least biomass and had the lowest N concentration among the four legumes studied (Fig. 7.1 B).
Thus, this *Sesbania* species, in spite of its photoperiod insensitivity (i.e., a potentially short-season, fast-growing legume) does not appear to be suited as a green manure crop when grown in acid sulfate soils. Furthermore, strong linear relationships between biomass and plant N concentration (Table 7.3) indicate that N nutrition partly controlled dry matter production, suggesting that either the symbiotic rhizobia and the host legume had similar responses to soil acidity and liming or the rhizobia were more susceptible to soil acidity. The latter possibility is more likely based on the facts that (i) both *S. speciosa* and *S. rostrata*, the two low-yielding legumes, always contained ≤ 3.0% N, a level considered inadequate for good growth, and (ii) the appropriate rhizobia for *S. speciosa* often fail under adverse environmental conditions as reported by Evans and Rotar (1987) and Dr. P. Prabuddham (personal communication) while the stem-nodulated rhizobia for *S. rostrata* might not have enough time to be fully active. This conclusion is supported by the work of Alva et al. (1986a) and Suthipradit (1989), who reported that rhizobial nodulation was more sensitive to Al toxicity than host plants, including soybean (*Glycine max*), cowpea (*Vigna unguiculata*), and green gram (*Vigna radiata*).

### 7.4.2 Soil acidity and chemical composition of the legumes

**Phosphorus.** Increasing soil pH from 3.9 to 6.5 steadily increased P concentration in the plants probably because of
Figure 7.1. Total N uptake (A) and plant N concentration (B) of the four green manure legumes grown in acid sulfate soils at different levels. CC : *Cajanus cajan*, SA : *Sesbania aculeata*, SR : *S. rostrata*; SS : *S. speciosa*. Vertical bars are standard errors. Unlimed pH is designed as 3.9 which is the average of 3.8 and 4.0, the actual pHs of the two unamended soils.
more vigorous growth at higher pH and because soil P becomes more available for plant uptake at pH range of 5.5 - 6.5. In *C. cajan*, plant P increased from 0.19% in the unamended soils to 0.30% at pH 5.5 and to 0.36% at pH 6.5 (Table 7.4). Given the plateauing of the dry-matter yield at pH 5.5 (Table 7.3), it appears that a plant P concentration of 0.30% would be adequate for *Cajanus cajan* growth. In fact, this P level agrees well with the adequate range of 0.30 - 0.35% P tabulated by Reuter and Robinson (1986) for this legume species sampled 60 days after sowing.

In the *Sesbania*, P increased steadily from 0.16% at pH 3.9 to about 0.30% at pH 5.5 then practically leveled off at higher pH (Table 7.4). Thus, 0.30% P also seems to be the adequate level for *Sesbania* species growth. Evans and Rotar (1987) also reported 0.30% P as a "normal" concentration in many *Sesbania* species and Singh et al. (1992) listed 0.32% as the average P concentration (with a range of 0.21 - 0.40%) in *S. aculeata*. In general, the four legume species behaved similarly in terms of P nutrition in response to soil acidity.

Potassium. Although herbage K increased steadily from 1.87% to 2.38% in *C. cajan* (the increases were not statistically significant, however), and fluctuated between 1.8 and 2.4% in *S. aculeata* and remained virtually constant at 1.9% in *S. rostrata* and 1.6% in *S. speciosa*, as lime rates increased (Table 7.4). Thus, in our experiment, soil acidity apparently had little effect on K nutrition of the legumes, perhaps
Table 7.4. Nutrient composition \(^1\) of four tropical legumes used as green manures as affected by different pH in two acid sulfate soils.

<table>
<thead>
<tr>
<th>Soil pH</th>
<th>Plant top composition</th>
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<tr>
<td></td>
<td></td>
<td>P</td>
<td>K</td>
<td>Ca</td>
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<tr>
<td></td>
<td></td>
<td>%</td>
<td>mg kg(^{-1})</td>
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<tr>
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<td>146</td>
<td>236</td>
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<tr>
<td>4.5</td>
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<td>2.03</td>
<td>0.77</td>
<td>0.92</td>
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<td>126</td>
<td>151</td>
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<td>1.22</td>
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<td>75</td>
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<td>32</td>
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<tr>
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<td>0.24</td>
<td>2.42</td>
<td>1.03</td>
<td>0.64</td>
<td>121</td>
<td>148</td>
<td>322</td>
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<tr>
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<td>0.30</td>
<td>1.89</td>
<td>1.18</td>
<td>0.98</td>
<td>76</td>
<td>133</td>
<td>228</td>
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</tr>
<tr>
<td>6.5</td>
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<td>2.36</td>
<td>1.25</td>
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<td>57</td>
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</tr>
<tr>
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<td>49</td>
<td>72</td>
<td></td>
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</tr>
</tbody>
</table>

\(^1\) Average of data from the two soils.
because K was supplied adequately by all the treatments. [Adequate concentration of K was reportedly ≥ 1.7% in C. cajan (Reuter and Robinson, 1986) and 1.6 - 1.8% in Sesbania species (Singh et al., 1992).

**Calcium.** Adding Ca(OH)₂ to raise the soil pH also raised plant Ca significantly (Table 7.4). In C. cajan, plant Ca increased linearly from 0.32% in the unamended treatment to 2.13% in the highest limed treatment. By assuming that Ca was the most limiting factor to the legume growth in the acid soils, a rough estimate of critical Ca levels was obtained by plotting the dry-matter yield vs. plant Ca (Fig. 7.2). This figure shows that 1.75% and 1.20% Ca would be required by C. cajan to maintain growth at 90% and 80% of the maximum, respectively. The lower value agrees well with the adequate range of 0.8 - 1.2% Ca reported by Reuter and Robinson (1986), and is probably closer to the "true" Ca requirement because under the Al toxicity stress (as in our case) Ca requirement has been shown to be higher than in the absence of such a stress (Alva et al., 1986b). On the other hand, Ca levels of 0.32% and 0.77% in plants of the unamended soils (pH 3.9) and the lowest lime treatment (pH 4.5) were clearly deficient, which were partially responsible for the observed poor growth.

Using the same approach, adequate Ca levels were identified as 0.82% for S. aculeata, 0.57% for S. rostrata, and 0.42% for S. speciosa (Fig. 7.2). Evans and Rotar (1987) also listed 0.8 - 1.1% Ca as the normal range for good Sesbania growth.
Figure 7.2. Relationship between dry-matter yield of the four green manure legumes and the Ca concentration in plant tops.

It is worth noting that the two high-yielding legumes (C. cajan and S. aculeata) were able to obtain and accumulate more Ca at each pH level than the other two low-yielding species (Table 7.4). For example, in the unamended soils, C. cajan and S. aculeata contained about 0.32% Ca as compared to 0.15% Ca
in *S. rostrata* and *S. speciosa*. Perhaps, the ability to efficiently absorb Ca from Ca-poor sources has made *C. cajan* and *S. aculeata* well adapted to acid soils of Thailand as our survey indicated.

**Magnesium.** In the unlimed treatment, *C. cajan* contained 0.47% Mg, *S. aculeata* 0.55%, *S. rostrata* 0.44%, and *S. speciosa* 0.38%. Despite these rather high initial concentrations, plant Mg did increase two to three fold as soil pH increased (Table 7.4). Given the fact that the soils were inherently high in Mg (Table 7.1) and that the adequate Mg level was ≤ 0.3% in both *C. cajan* (Reuter and Robinson, 1986) and *S. sesban* (Singh et al., 1992), this Mg increase was due mainly to a more vigorous growth of the legumes at higher pH and at better Ca supplies. Since Mg was not a growth limiting factor, its uptake pattern among the four legume species was not clearly different, except that Mg in the two high-yielding species seems to increase steadily with liming while Mg in the two low-yielding species seems to level off at 1.0% (*S. rostrata*) and 0.6% (*S. speciosa*).

**Iron and Manganese.** The four legumes responded differently to the potentially excessive Fe in the acid sulfate soils (Fig. 7.3). *C. cajan* accumulated only 236 mg Fe kg⁻¹ in the unlimed soils and maintained its internal Fe between 151 and 81 mg kg⁻¹ as lime quantities were added to raise the soil pH to 4.5 and 6.5 (Table 7.4). According to Reuter and Robinson (1986), Fe concentrations are considered adequate for *C. cajan*
Figure 7.3. Plant Fe and Mn concentrations in the four green-manure legumes as a function of soil pH. Vertical bars are standard errors.
growth at 150 - 190 mg Fe kg\(^{-1}\), and would not be deficient unless < 60 mg Fe kg\(^{-1}\). Thus, it seems logical to speculate that *C. cajan* has an ability to regulate Fe uptake and to prevent Fe from becoming detrimental to its metabolism when grown on acid sulfate soils. By contrast, *S. rostrata* and particularly *S. speciosa*, accumulated between 513 and 616 mg Fe kg\(^{-1}\) when grown on the unlimed soils (Table 7.4). Whether these high Fe levels were a result or a cause of poor growth (low dry matter yield) could not be resolved in this experiment because the data were taken only at harvest (after 7 weeks of growth). It is clear however, that the two high-yielding legumes (*C. cajan* and *S. aculeata*) always had lower Fe concentration than the other two low-yielding legumes, especially at the two lowest soil pH levels of 3.9 and 4.5 (Fig. 7.3).

Plant Mn shows a response pattern similar to plant Fe: lowest in the high-yielding *C. cajan* and *S. aculeata* and highest in the low yielding *S. rostrata* and *S. speciosa* (Table 7.4 and Fig. 7.3). This observation agrees well with that made by Nakano et al. (1992) in explaining a high biomass production of *C. cajan* as compared to *S. rostrata* and *Crotalaria juncea*, when grown in acid red soil of southern Japan. The differences in Mn concentrations in the four legumes were however, smaller than those of Fe; and absolute Mn concentrations were all below 275 mg kg\(^{-1}\). Since Mn levels in *C. cajan* would not be detrimental until they exceeded 300
Mg kg⁻¹ (Reuter and Robinson, 1986), it is unlikely that Mn was a cause of poor growth for any legume in this experiment. Thus, the greater accumulation of Mn by the low-yielding legumes than their high-yielding counterparts might have been due to their genetic differences because even at pH 6.5 where dry matter yields were relatively high, *S. speciosa* and *S. rostrata* still contained 162 and 144 mg Mn kg⁻¹, respectively, nearly twice the Mn concentration in *C. cajan* (88 mg kg⁻¹) and *S. aculeata* (71 mg kg⁻¹).

**Aluminum.** Given the high exchangeable Al in these acid sulfate soils (Table 7.1), Al phytotoxicity was likely when no lime was added. In fact, in the unlimed soils, all four legumes contained 140 to 175 mg Al kg⁻¹, which subsequently declined exponentially as lime rates increased, a typical response of a living organism to a toxicant (Table 7.4). At pH 6.5, plant Al was 37 mg kg⁻¹ in *S. speciosa* and 75 mg kg⁻¹ in *C. cajan*. Regarding the Al toxicity threshold, we found no published data for the legumes used in this study. In a published abstract, however, Licudine and Hue (1992) suggested that Al levels ≥ 40 mg kg⁻¹ and ≥ 85 mg kg⁻¹ would reduce dry matter yield of 6-week-old *S. cochinchinensis* by 10% and 50%, respectively. Similarly, Hilyar (1979) related Al toxicity to concentrations exceeding 40 mg Al kg⁻¹ in soybeans at 43 days after planting. It is worth noting that these reported critical Al levels were in the lower limit of Al concentrations found in our experimental plants even at pH 6.5.
In our experiment, however, defining the critical Al concentration is not simple because Ca was also affecting growth. It has been well accepted that Ca strongly interacts with Al in terms of ameliorating Al phytotoxicity (Alva et al., 1986b). To deal with this Ca/Al interaction, we plotted the relative yield of each legume as a function of its Ca/Al ratio (Fig. 7.4). Such plots show that approximately 80% of the variation in the dry matter yield could be attributed to Ca/Al ratios in the plants. Also, relative yields would attain ≥ 90% of the maximum if Ca/Al equals 150 for *C. cajan* and *S. speciosa*, 200 for *S. rostrata*, and 300 for *S. aculeata* (Fig. 7.4). Based on Ca levels of 1.25% for *C. cajan*, 0.82% for *S. aculeata*, 0.57% for *S. rostrata*, and 0.42% for *S. speciosa*, that were considered minimum requirements for adequate growth of these respective species (Fig. 7.2), we estimated that critical Al concentration, above which significant yield reductions would be expected, was 80 mg kg⁻¹ for *C. cajan*, 40 mg kg⁻¹ for *S. rostrata*, and 33 mg kg⁻¹ for both *S. aculeata* and *S. speciosa*. Thus *C. cajan* apparently was the most Al tolerant while the three *Sesbania* species had similar Al-toxicity but different Ca-deficiency tolerances.

### 7.5 Summary and conclusions

Increasing use of fast growing legumes as green manure for improving soil productivity and crop production necessitates an evaluation of their adaptability to acid soils, especially
to acid sulfate soils which occupy a major portion of Thailand’s coastal areas. Based on green manuring criteria of high biomass production and high N content, *C. cajan* and *S. aculeata* were better suited to the acid soils than *S. rostrata* and *S. speciosa*. Since dry-matter increases were most pronounced in the pH range of 4.5 - 5.5, liming to pH ~ 5.5
was recommended for the growth of these legumes after taking a cost/benefit analysis into consideration. (In many developing countries where green manures are most needed, lime may be expensive or not readily available because of poor infrastructure. Thus a small yield increase after pH 5.5 might not cover the lime cost.).

The legumes responded differently to stresses imposed by soil acidity: *C. cajan* and *S. aculeata* were able to absorb much more Ca but much less Fe and Mn than the other two legumes. Calcium concentrations required for adequate growth were estimated to be 1.2% for *C. cajan*, 0.8% for *S. aculeata*, 0.6% for *S. rostrata* and 0.4% for *S. speciosa*. Although the four legumes had similar P and K uptake patterns, *C. cajan* could tolerate nearly three times the levels of Al as the *Sesbania*: critical Al concentrations (for 10% dry-matter reduction) were 80 mg kg\(^{-1}\) for the former and 33 - 40 mg kg\(^{-1}\) for the latter.
References


Biological Nitrogen Fixation Associated with Rice Production. CRRI. Cuttack, India.


XXXXXXXXX
CHAPTER 8

Ameliorating aluminum toxicity in upland rice grown on acid sulfate soils, using green manures

8.1 Abstract

Green manuring reportedly can reduce Al toxicity in acid soils. A greenhouse experiment was conducted to quantitatively compare the effects of two green manures and lime on Al detoxification in upland rice (Oryza sativa L. var. RD 15) grown on two acid sulfate soils. The soils used were Bg (Typic Sulfaquents) and Ra (Sulfic Tropaquepts) from the Bangkok Plain with initial pH 3.8 and 4.0, respectively. Treatments were 0, 4, 8 Mg CaCO₃ ha⁻¹, and 0, 20, 40 and 80 Mg ha⁻¹ ground tops of sesbania (Sesbania aculeata) or pigeon pea (Cajanus cajan). Plant height, shoot and root dry weight, and relative root length of rice plants at 60 days were measured. Soil solutions were analyzed at harvest.

The results indicated that green manure applications effectively detoxified Al. Pigeon pea was better than sesbania in reducing Al³⁺ activities in the soil solution. Major chemical processes were increased soil solution pH, EC, Ca and Mg, followed by precipitation of soluble Al and/or the formation of Al-organic complexes.

Rice plants were moderately tolerant of Al toxicity. Nevertheless, Al⁺³, Al(SO₄)²⁻ and Alₙₐₙ activities in the soil solution were strongly correlated with rice growth. Relative
root length predicted rice growth better than plant height, dry weights of shoots and roots. Soil solution attributes \([\text{Al}^{3+}, \text{Al}(\text{SO}_4)^{2-} \text{and Al}_{\text{sum}}]\) were good indicators of Al toxicity.

Green manure amendments and CaCO\(_3\) treatments were compared by estimating the amounts of the materials required to decrease Al\(^{3+}\) activity until relative root length of rice plants was \(\geq 90\%\). The rates of CaCO\(_3\), pigeon pea and sesbania applications required to reach this critical level were 5.3, 44.4, 57.5 Mg ha\(^{-1}\), respectively.

8.2 Introduction

Acid sulfate soils are developed from pyrite oxidation when the soils are exposed to air after drainage. These soils are characterized by very low pH and high Al concentrations, and by yellowish jarositic mottles in the B and/or Ap horizons (van Breemen, 1982). In the Bangkok Plain of Thailand, there are approximately 900,000 ha of both actual and potential acid sulfate soils, of which 80% are under rice cultivation (Charoenchamratratcheep et al., 1987).

Al toxicity is a major constraint to rice growth on acid sulfate soils (Moore et al., 1990). Rice grows poorly in these soils if the pyritic layer occurs within the top meter (Satawathananont et al., 1991). Strategies used for ameliorating acid sulfate soils include liming, flooding, and organic amendments. Liming to raise soil pH and to precipitate Al has been a common practice to alleviate surface soil
acidity, but the movement of surface-applied lime (CaCO₃) down the soil profile is extremely limited. Therefore, surface liming has little effect on Al toxicity in the subsoils. Furthermore, lime may not be available nor affordable by subsistence farmers of the tropics. Flooding is not possible for upland rice.

An alternative to lime for reducing Al toxicity is the use of organic amendments. Additions of organic materials to acid soils could prevent Al toxicity (Hoyt and Turner, 1975; Hargrove, 1986). Evans and Kamprath (1970) found that as the organic matter content of the soil increased, less Al³⁺ was present in the soil solution at a given pH. It is believed that Al ions are detoxified by interactions with organic matter to form Al-organo complexes and chelates (Cabrera and Talibudeen, 1977). Hue et al. (1986) and Suthipradit et al. (1990) have shown that soluble organically complexed Al is nonphytotoxic.

Additions of ground leaves of some legumes to acid soils from Hawaii reduced Al toxicity and increased plant growth (Hue and Amien, 1989), and such applications should be tested on acid sulfate soils. Thus, the objectives of this study were (i) to quantify changes in soil-solution compositions of acid sulfate soils as affected by lime or green manure applications, and (ii) to measure rice responses to these soil amendments.
8.3 Materials and methods

8.3.1 Soils and organic amendments

Soil samples were collected from cultivated paddy areas representing two soil series: Bang Pakong (Bg), and Rangsit very acid phase (Ra). The Bg soil was a preoxidized potential acid sulfate soil (Typic Sulfquents); the Ra soil was an actual acid sulfate soil (Sulfic Tropaquepts). The soils were air-dried, and ground to pass a 2-mm sieve. Selected physical and chemical properties of the soils are listed in Table 8.1.

Sesbania aculeata and pigeon pea (Cajanus cajan) were selected as green manures for soil amendments because a previous study has shown that these legumes adapted well to acid sulfate soils (Chapter 7). Leaves and stems were chopped to approximately 1 cm, oven dried at 70 °C, ground to < 1 mm, mixed and stored at room temperature in air-tight containers until use. Nutritional values (%) of the green manures are: (Sesbania 3.20 N, 0.25 P, 2.12 K, 0.94 Ca and 0.93 Mg; pigeon pea 3.22 N; 0.26 P, 2.13 K, 1.14 Ca and 1.01 Mg).

8.3.2 Plant growth study

The pot experiment had a factorial design with 3 replications. Treatments included lime rates equivalent to 0, 4, and 8 Mg CaCO	extsubscript{3} ha	extsuperscript{-1} and 4 rates of the green manures 0, 10, 20, and 40 g kg	extsuperscript{-1}, which were equivalent to 0, 20, 40, and 80 Mg ha	extsuperscript{-1}, respectively. Basal nutrients (in mg kg	extsuperscript{-1} soil: Na	extsubscript{2}MoO	extsubscript{4}.2H	extsubscript{2}O, 0.67; H	extsubscript{3}BO	extsubscript{3}, 0.83; CuSO	extsubscript{4}.5H	extsubscript{2}O, 5; ZnSO	extsubscript{4}.7H	extsubscript{2}O, 10;
Table 8.1. Some selected physical and chemical properties of the two unamended acid sulfate soils used in the greenhouse experiment.

<table>
<thead>
<tr>
<th>Soil properties</th>
<th>Soil Series</th>
<th>Bang Pakong</th>
<th>Rangsit</th>
</tr>
</thead>
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<tr>
<td>pH (1:1; soil : water)</td>
<td></td>
<td>3.8</td>
<td>4.0</td>
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<tr>
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<td>Organic carbon (%)</td>
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<td>2.2</td>
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<tr>
<td>Extractable P (mg kg⁻¹)</td>
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<td>8.4</td>
<td>9.0</td>
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<td>CEC (cmolₑ kg⁻¹)</td>
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<td>Exchangeable K (cmolₑ kg⁻¹)</td>
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<td>4.3</td>
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<td>711.1</td>
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<tr>
<td>DTPA-Extractable Mn (mg kg⁻¹)</td>
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<tr>
<td>Water soluble SO₄²⁻ (mgS kg⁻¹)</td>
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<td>Particle size distribution</td>
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<td>35.6</td>
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<tr>
<td>Clay (%)</td>
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<td>56.8</td>
<td>61.7</td>
</tr>
</tbody>
</table>

¹/ Bray P-II method
²/ 1 M NH₄OAc, pH 7.0 method

MnSO₄·H₂O, 15; KH₂PO₄, 176) were applied to all pots. Nitrogen was also applied at 24 mg N kg⁻¹ as NH₄NO₃. Each pot contained 2 kg of air-dried soils. The pots were placed randomly in the greenhouse and incubated for 21 days at field water holding capacity.
Upland rice var. RD 15 was planted at the rate of 6 seeds per pot, and thinned to 3 seedlings 7 days later. Thereafter, the pots were moistened to field water holding capacity daily. The plants were allowed to grow for 60 days after germination. Plant height and tiller shoot dry weight were determined. Roots were carefully separated from the adhering soil. The shoots and roots were oven dried for 48 h at 70 °C, weighed, ground and digested for chemical analysis. Total N was analyzed by the micro Kjeldahl method. Total Al, Ca, K, Fe and Mn in the digest were determined by atomic absorption spectrophotometry (AAS). The data obtained were subjected to analysis of variance, and the differences among means were evaluated by the LSD (0.05) test.

8.3.3 Soil-solution collection and analysis

The air-dried soil samples from various treatments after harvest were rewetted with distilled water to field capacity, and equilibrated for 24 hr. The soil solution was extracted by a centrifuge method (Menzies and Bell, 1988). Extracted soil solution was filtered through a 0.45 µm membrane, and pH and electrical conductivity (EC) were measured immediately. The rest of the soil solution was analyzed for Ca, Mg, K, Na, \( \text{SO}_4^{2-} \), P and \( \text{NO}_3^- \). Calcium, Mg, K and Na were measured with AAS. Phosphorus and \( \text{NO}_3^- \) were determined colorimetrically using a Technicon Auto-Analyzer II. \( \text{SO}_4^{2-} \) was measured turbidimetrically at 420 nm (Freeney, 1986). Total dissolved
organic C in the soil solution was determined by the method of Bartlett and Ross (1988). Total Al in the soil solution was determined by the catechol violet method (Kerven et al., 1989). Analytical data from the soil solution were used to calculate ionic strength (I) and single-ion activities. The calculation of ionic strength was based on EC of the soil solutions (Griffin and Jurinak, 1973). The single-ion activities were computed from the measured pH, EC and concentrations of each element by the SOILSOLN computer program (Wolt, 1987). Speciation of monomeric Al was calculated by taking into account complex formation of Al with SO$_4^{2-}$ (all S measured in this experiment was regarded as sulfate), OH$^-$, and soluble carbon.

### 8.4 Results and discussion

#### 8.4.1 Effects of lime and green manure amendments on chemical properties of the soil solution

**pH and electrical conductivity.**Although the initial pH values of the soils were very low (3.8 - 4.0), significant increases in pH and EC were resulted from the amendments (Table 8.2). Soil solution pH increased to 5.2 in the Bg soil and to 5.4 in the Ra soil when CaCO$_3$ was applied at 8 Mg ha$^{-1}$. The pigeon pea and sesbania additions at the highest rates of 80 Mg ha$^{-1}$ also increased soil pH to 5.0 and 5.6. Pigeon pea seemed more effective (5 - 9 %) than Sesbania as green manures in raising soil pH. A similar effect of organic materials on increasing soil pH was noted by Ritchie and Dolling (1985) for
Table 8.2. Chemical properties of the soil solution as affected by various levels of CaCO\(_3\) (Ca), sesbania (Ses) and pigeon pea (Pea) application to two acid sulfate soils.

<table>
<thead>
<tr>
<th>Soils/Treatments</th>
<th>pH</th>
<th>EC (dS m(^{-1}))</th>
<th>Ionic strength (mM)</th>
<th>K (µM)</th>
<th>Ca (µM)</th>
<th>Mg (µM)</th>
<th>Na (µM)</th>
</tr>
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<tbody>
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<td>Bg</td>
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</tr>
<tr>
<td>Ca 0</td>
<td>4.3</td>
<td>1.4</td>
<td>18.2</td>
<td>569</td>
<td>424</td>
<td>866</td>
<td>1320</td>
</tr>
<tr>
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<td>4.9</td>
<td>1.7</td>
<td>22.1</td>
<td>1030</td>
<td>676</td>
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<td>1850</td>
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<tr>
<td>Ca 8</td>
<td>5.2</td>
<td>1.9</td>
<td>24.7</td>
<td>1210</td>
<td>907</td>
<td>1590</td>
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<td>1.5</td>
<td>19.5</td>
<td>742</td>
<td>632</td>
<td>888</td>
<td>1645</td>
</tr>
<tr>
<td>Ses 40</td>
<td>4.7</td>
<td>1.6</td>
<td>20.8</td>
<td>875</td>
<td>586</td>
<td>1255</td>
<td>1772</td>
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<tr>
<td>Ses 80</td>
<td>5.0</td>
<td>1.8</td>
<td>23.4</td>
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<tr>
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<td>1.8</td>
<td>23.4</td>
<td>999</td>
<td>735</td>
<td>1360</td>
<td>1770</td>
</tr>
<tr>
<td>Pea 40</td>
<td>4.9</td>
<td>1.7</td>
<td>22.1</td>
<td>1029</td>
<td>1029</td>
<td>1494</td>
<td>1851</td>
</tr>
<tr>
<td>Pea 80</td>
<td>5.4</td>
<td>2.1</td>
<td>27.3</td>
<td>1248</td>
<td>948</td>
<td>1757</td>
<td>1900</td>
</tr>
<tr>
<td>LSD(_{0.05})</td>
<td>0.1</td>
<td>0.1</td>
<td>1.8</td>
<td>77</td>
<td>79</td>
<td>103</td>
<td>93</td>
</tr>
</tbody>
</table>

| Ra               |     |                     |                     |       |        |        |        |
| Ca 0             | 4.5 | 1.6                 | 20.8                | 841   | 808    | 1232   | 1607   |
| Ca 4             | 5.0 | 1.9                 | 24.7                | 1144  | 1135   | 1554   | 1838   |
| Ca 8             | 5.4 | 2.2                 | 28.6                | 1440  | 1386   | 1843   | 2208   |
| Ses 20           | 4.7 | 1.7                 | 22.1                | 908   | 887    | 1445   | 1717   |
| Ses 40           | 4.8 | 1.8                 | 23.4                | 1107  | 1109   | 1265   | 1827   |
| Ses 80           | 5.3 | 2.2                 | 28.6                | 1482  | 1259   | 1469   | 1834   |
| Pea 20           | 5.0 | 1.9                 | 24.7                | 1116  | 1106   | 1650   | 1925   |
| Pea 40           | 5.2 | 2.0                 | 26.0                | 1358  | 1278   | 1893   | 2178   |
| Pea 80           | 5.6 | 2.4                 | 31.2                | 1455  | 1509   | 2344   | 2441   |
| LSD\(_{0.05}\)    | 0.1 | 0.1                 | 2.1                 | 113   | 85     | 96     | 97     |

\(^{\dagger}\) Application rates of CaCO\(_3\) : 0, 4, 8 Mg ha\(^{-1}\)

\(^{\ddagger}\) Application rates of sesbania and pigeon pea : 0, 20, 40, 80 Mg ha\(^{-1}\)

\(^{\S}\) \(I \text{ (mM)} = 13 \times \text{EC (dS m}^{-1}\text{)}\)
lucern (*Medicago sativa*), and by Hue and Amien (1989) for cowpea (*Vigna unguiculata*), and leucaena (*Leucaena leucocephala*). Various reasons for such pH increases have been proposed, e.g., production of OH⁻ by (1) dissolution of solid Fe oxides in reduced conditions or (2) ligand exchange occurring through the replacement of terminal OH⁻ of Al and Fe-hydroxy oxides by organic anions (Hue and Amien, 1989).

Soil-solution EC of the unamended soils was 1.4 - 1.6 dS m⁻¹, which increased to 1.7 - 2.2 dS m⁻¹ in the lime treatments and 1.5 - 2.4 dS m⁻¹ in the green manure treatments (Table 8.2). The increases in EC in the sesbania and pigeon pea treatments were related to the substantial amounts of nutrients in these materials. Higher EC in the pigeon pea treatments than the sesbania treatments presumably resulted from the higher Ca and Mg contents of the pigeon pea.

**Basic cations.** Soil-solution Ca and Mg concentrations increased significantly with lime and green manure additions (Table 8.2). Additions of 4 and 8 Mg ha⁻¹ of CaCO₃ increased soil-solution Ca by 252 - 578 μM, Mg by 322 - 724 μM. Additions of 20 to 80 Mg ha⁻¹ green manure increased Ca by 22 - 644 μM and Mg by 7 - 1204 μM. The increases in K (54 - 601 μM) and in Na (7 - 863 μM) in the CaCO₃ treatments might have resulted from Ca replacing K and Na on the exchange complex. The changes in K concentration in the green manure treatments were probably due to both the direct contribution of K by the green manures and the exchange of K with added Ca, Mg on the
soil surfaces. Regardless of the reactions involved, liming or green manuring improved the availability of Ca, Mg and K, making the soils more favorable for plant growth.

**Sulfate and phosphate concentrations.** The concentration of SO₄²⁻ in the soil solution increased significantly with increasing rates of CaCO₃ or green manures (Table 8.3). In the CaCO₃ treatments (4 - 8 Mg ha⁻¹), SO₄²⁻ increased by 618 to 1527 μM in both acid sulfate soils which had jarositic layers close to the soil surface. The jarositic layer contained sulfur-bearing minerals, which dissolved as pH increased (De Coninck, 1978). This explanation also seems applicable to the green manure treatments. A sulfate increase in the Ra soil from approximately 2500 μM to nearly 4500 μM with the application of 80 Mg ha⁻¹ of pigeon pea was caused mainly by an increase in soil-solution pH from 4.6 to 5.6 (Table 8.3). Although these high SO₄²⁻ levels are not uncommon in acid sulfate soils, they are about 10 times more than the level needed by many crops for normal growth (Hue et al., 1984). The role of excessive SO₄²⁻ in P availability and Al toxicity warrants closer investigation.

Soil-solution P increased from 1.5 μM to 2.1 and 2.5 μM in the Bg soil, and from 2.6 μM to 3.7 and 4.8 μM in the Ra soil as 4 and 8 Mg CaCO₃ ha⁻¹ were applied, respectively. It is reasonable to believe that liming reduced positive charge on the soil particle surfaces as well as concentration of Al and Fe in the soil solution (discussed later). Thus, lesser
Table 8.3. Chemical properties of the soil solution as affected by various levels of CaCO$_3$ (Ca), sesbania (Ses) and pigeon pea (Pea) application to two acid sulfate soils.

<table>
<thead>
<tr>
<th>Soils/ Treatments</th>
<th>pH</th>
<th>Total Al</th>
<th>Fe</th>
<th>Mn</th>
<th>P</th>
<th>SO$_4^{2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bg</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca 0 †</td>
<td>4.3</td>
<td>345.6</td>
<td>55.9</td>
<td>23.2</td>
<td>1.5</td>
<td>1789</td>
</tr>
<tr>
<td>Ca 4</td>
<td>4.9</td>
<td>99.0</td>
<td>28.2</td>
<td>13.4</td>
<td>2.1</td>
<td>2408</td>
</tr>
<tr>
<td>Ca 8</td>
<td>5.2</td>
<td>85.8</td>
<td>18.8</td>
<td>10.3</td>
<td>2.5</td>
<td>2882</td>
</tr>
<tr>
<td>Ses 20 ‡</td>
<td>4.5</td>
<td>188.9</td>
<td>43.9</td>
<td>19.5</td>
<td>1.7</td>
<td>1917</td>
</tr>
<tr>
<td>Ses 40</td>
<td>4.7</td>
<td>129.2</td>
<td>32.1</td>
<td>15.4</td>
<td>1.9</td>
<td>2209</td>
</tr>
<tr>
<td>Ses 80</td>
<td>5.0</td>
<td>108.4</td>
<td>24.9</td>
<td>11.2</td>
<td>2.2</td>
<td>2555</td>
</tr>
<tr>
<td>Pea 20 ‡</td>
<td>4.9</td>
<td>133.2</td>
<td>28.0</td>
<td>14.9</td>
<td>2.2</td>
<td>2413</td>
</tr>
<tr>
<td>Pea 40</td>
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<td>12.2</td>
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<td>2516</td>
</tr>
<tr>
<td>Pea 80</td>
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<td>17.2</td>
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</tr>
<tr>
<td>LSD$_{0.05}$</td>
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<td>2.5</td>
<td>0.2</td>
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</tr>
<tr>
<td>Ra</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca 0</td>
<td>4.5</td>
<td>267.5</td>
<td>41.0</td>
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</tr>
<tr>
<td>Ca 4</td>
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<td>132.5</td>
<td>21.3</td>
<td>11.4</td>
<td>3.7</td>
<td>3355</td>
</tr>
<tr>
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<td>5.4</td>
<td>76.2</td>
<td>15.7</td>
<td>9.2</td>
<td>4.8</td>
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</tr>
<tr>
<td>Ses 20</td>
<td>4.7</td>
<td>193.5</td>
<td>32.2</td>
<td>16.1</td>
<td>3.1</td>
<td>2897</td>
</tr>
<tr>
<td>Ses 40</td>
<td>4.8</td>
<td>164.5</td>
<td>24.4</td>
<td>11.9</td>
<td>3.4</td>
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<tr>
<td>Ses 80</td>
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<td>107.7</td>
<td>17.6</td>
<td>10.4</td>
<td>4.5</td>
<td>3891</td>
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<tr>
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<td>144.3</td>
<td>22.4</td>
<td>10.5</td>
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<td>18.3</td>
<td>10.0</td>
<td>4.1</td>
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<tr>
<td>Pea 80</td>
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<td>78.7</td>
<td>14.1</td>
<td>7.9</td>
<td>5.4</td>
<td>4497</td>
</tr>
<tr>
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<td>4.8</td>
<td>2.0</td>
<td>0.4</td>
<td>348</td>
</tr>
</tbody>
</table>

† Application rates of CaCO$_3$: 0, 4, 8 Mg ha$^{-1}$

‡ Application rates of sesbania and pigeon pea: 0, 20, 40, 80 Mg ha$^{-1}$
amounts of the added P were adsorbed or precipitated and more P remained in the soil solution.

Adding organic manures also increased P substantially (Table 8.3). Pigeon pea was the most effective, and sesbania the least among the three amendments in increasing soil-solution P. For example, the 80 Mg ha$^{-1}$ treatment of the pigeon pea doubled P concentration from 2.6 $\mu$M to 5.4 $\mu$M in the Ra soil. Besides raising soil pH as with liming, organic manures could also increase solution P via their direct P contributions and via producing organic molecules that can compete effectively with P for sorption sites on the soil particle surfaces (Hue, 1991; 1992).

Since rice is known to adapt well to relatively P-depleted soils (R.L. Fox, personal communication), and given the external P requirements of related plant species (e.g., corn and sorghum) as 1.6 - 1.9 $\mu$M for 95 % maximum yields (Fox, 1979), P did not appear to limit rice growth in this experiment, especially in those treatments receiving lime or green manures.

**Total Al concentrations in soil solution.** There was a decrease in total Al concentration from 345.6 $\mu$M to 65.8 $\mu$M in the Bg soil, and from 267.5 $\mu$M to 76.2 $\mu$M in the Ra soil with an increase in soil solution pH (4.3 - 5.4) by the CaCO$_3$ treatments. An exponential equation of $Y = a \cdot \exp(bx)$ was fitted to the regression of total Al concentration and pH for both soils. In general, Al concentration in the soil solution was
negatively correlated with pH ($r^2 = 0.89^{**}$). When pH was raised to 5.2 - 5.4 after applications of 8 Mg CaCO$_3$ ha$^{-1}$ to both acid sulfate soils, the total Al concentration was reduced to 65.8 - 76.2 μM, a level considered as nontoxic to a moderately acid tolerant plant such as upland rice (Table 8.3). Liming, therefore, is an important agronomic practice for crop production on acid sulfate soils, although it may be costly. Liming has been shown experimentally to be successful with rice, corn, and tropical fruit trees in the Bangkok Plain (Muensangk, 1991).

The pigeon pea treatments decreased total Al concentrations similarly to the CaCO$_3$ treatments (Table 8.3). On the other hand, the sesbania treatments resulted in higher total Al concentrations than the pigeon pea treatments at the same application rate. Nevertheless, application of sesbania at 80 Mg ha$^{-1}$ significantly reduced total Al concentration in the soil solution.

**Al speciation and activities in soil solution.** Table 8.4 lists the activities of various Al species, Mn, and SO$_4$ as calculated by the SOILSOLN computer program (Wolt, 1987). Aluminum species existed principally in the soil solution as Al$^{3+}$ and as complexes with SO$_4^{2-}$ and OH$^-$. Addition of various treatments decreased Al activities in a similar manner to that observed with total Al concentrations, although the activities were approximately 14.4% of the total Al concentration on average. The decrease in Al$^{3+}$ activity in both acid sulfate
Table 8.4. Calculated activities of monomeric Al species and sulfate in the soil solution as affected by various levels of CaCO$_3$ (Ca), sesbania (Ses) and pigeon pea (Pea) application to two acid sulfate soils.

<table>
<thead>
<tr>
<th>Soils/ Treatments</th>
<th>pH</th>
<th>Al$^{3+}$</th>
<th>Al(OH)$^{+2}$</th>
<th>Al(OH)$_2^+$</th>
<th>Al(OH)$_3^+$</th>
<th>Al$_{salt}$</th>
<th>Mn</th>
<th>SO$_4^{2-}$</th>
</tr>
</thead>
<tbody>
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<td>Bg</td>
<td></td>
<td>($\mu$M)</td>
<td>($\mu$M)</td>
<td>($\mu$M)</td>
<td>($\mu$M)</td>
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<tr>
<td>Ca 0</td>
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<td>55.9</td>
<td>13.7</td>
<td>18.5</td>
<td>0.9</td>
<td>91.0</td>
<td>180.1</td>
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</tr>
<tr>
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<td>30.7</td>
<td>5.8</td>
<td>14.8</td>
<td>64.8</td>
<td>8.9</td>
</tr>
<tr>
<td>Ca 8</td>
<td>5.2</td>
<td>1.4</td>
<td>2.8</td>
<td>31.4</td>
<td>13.3</td>
<td>3.4</td>
<td>52.5</td>
<td>6.6</td>
</tr>
<tr>
<td>Ses 20 $^\dagger$</td>
<td>4.5</td>
<td>26.1</td>
<td>9.5</td>
<td>19.2</td>
<td>1.5</td>
<td>44.4</td>
<td>100.9</td>
<td>13.1</td>
</tr>
<tr>
<td>Ses 40</td>
<td>4.7</td>
<td>12.9</td>
<td>8.0</td>
<td>27.6</td>
<td>3.6</td>
<td>24.9</td>
<td>77.3</td>
<td>10.2</td>
</tr>
<tr>
<td>Ses 80</td>
<td>5.0</td>
<td>5.9</td>
<td>6.6</td>
<td>40.6</td>
<td>9.6</td>
<td>12.9</td>
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<tr>
<td>Pea 20 $^\ddagger$</td>
<td>4.9</td>
<td>9.3</td>
<td>8.4</td>
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<td>8.1</td>
<td>19.3</td>
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<td>1.7</td>
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</tr>
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<td>($\mu$M)</td>
<td>($\mu$M)</td>
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</tr>
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<td>2.3</td>
<td>72.9</td>
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<td>95.1</td>
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</tr>
<tr>
<td>Ca 8</td>
<td>5.4</td>
<td>0.7</td>
<td>2.2</td>
<td>36.0</td>
<td>22.9</td>
<td>2.4</td>
<td>64.3</td>
<td>5.7</td>
</tr>
<tr>
<td>Ses 20</td>
<td>4.7</td>
<td>17.8</td>
<td>11.1</td>
<td>38.4</td>
<td>5.1</td>
<td>44.3</td>
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<td>10.2</td>
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<tr>
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<td>4.8</td>
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<td>9.9</td>
<td>45.2</td>
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<td>31.1</td>
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<tr>
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<td>1.6</td>
<td>3.8</td>
<td>51.2</td>
<td>26.4</td>
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<td>20.8</td>
<td>100.7</td>
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<td>4.9</td>
<td>50.5</td>
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<td>Pea 80</td>
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<td>1.2</td>
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<td>38.3</td>
<td>0.9</td>
<td>69.8</td>
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</table>

$^\dagger$ Application rates of CaCO$_3$: 0, 4, 8 Mg ha$^{-1}$

$^\ddagger$ Application rates of sesbania and pigeon pea: 0, 20, 40, 80 Mg ha$^{-1}$

$^\ddagger$ Al$_{salt}$ = Sum of all monomeric Al species
soils was significantly related to soil solution pH (Fig. 8.1). Aluminum activities vs. pH in all treatments, can be described by the relationship: (Al in μΜ) = 1.1(10^8) \* exp(-3.34*soil solution pH) (r^2 = 0.98**). The reduction in Al^3+ activities by plant material application has been reported by Bell and Edwards (1987). Strong relationships between Al activity and soil solution pH for the green manure and CaCO₃ treatments in the present experiment indicate that the major effect of the green manures on Al may have been through pH increase and Al precipitation. The pH increase could also make native organic matter to complex Al more strongly.

The relative proportions of Al species with Al\text{sum} activities were also related to soil solution pH (Table 8.4). In the unamended soils, Al^{3+} was 22 - 31% of total Al activity, only surpassed by Al(SO₄)^{2-} (48.9 - 50.5%). When soil solution pH was raised to about 4.9 by either 4 Mg CaCO₃ ha⁻¹ or 40 Mg sesbania ha⁻¹ or 20 Mg pigeon pea ha⁻¹, Al^{3+} decreased to less than 10.6 - 11.3% of the Al\text{sum} activities.

**Basic cation activities in soil solution.** In the unamended treatments, the activities of K were 512 - 741 μΜ and Na 1202 - 1445 μΜ, which were rather high. Applications of CaCO₃ or green manures released even more of the cations into the soil solution (Table 8.5). The applications of CaCO₃ at 4 - 8 Mg ha⁻¹ markedly raised Ca activities from 158 μΜ to 326 μΜ, and also increased the other cation activities. When the soils were
$Y = 1.1 \times 10^8 \exp(-3.34 \text{Soil pH})$

$r^2 = 0.98^{**}$

**Figure 8.1.** Relationship between Al$^{3+}$ activity and soil solution pH as affected by all treatments for two acid sulfate soils.

limed with 8 Mg CaCO$_3$ ha$^{-1}$, increases in the activities of Ca$^{2+}$ and SO$_4^{2-}$ may result in a precipitation of gypsum (CaSO$_4$.2H$_2$O). The formation of gypsum in acid sulfate soil via this mechanism had been reported (De Coninck, 1978).

In the case of pigeon pea treatments, Mg activity increased in the range of 309 μM - 686 μM with increasing application rates from 20 to 80 Mg ha$^{-1}$. In the sesbania treatments of 20 - 80 Mg ha$^{-1}$, large increases in activities of K (54 - 559 μM)
Table 8.5. Calculated activities of basic cations in the soil solution as affected by various levels of CaCO₃ (Ca), sesbania (Ses) and pigeon pea (Pea) application to two acid sulfate soils.

<table>
<thead>
<tr>
<th>Soils/ Treatments</th>
<th>pH</th>
<th>Ca²⁺ (μM)</th>
<th>Mg²⁺ (μM)</th>
<th>K⁺ (μM)</th>
<th>Na⁺ (μM)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bg</strong></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>977</td>
<td>933</td>
<td>1659</td>
</tr>
<tr>
<td>Pea 20 ²</td>
<td>4.9</td>
<td>478</td>
<td>912</td>
<td>891</td>
<td>1584</td>
</tr>
<tr>
<td>Pea 40</td>
<td>4.9</td>
<td>524</td>
<td>977</td>
<td>912</td>
<td>1659</td>
</tr>
<tr>
<td>Pea 80</td>
<td>5.4</td>
<td>602</td>
<td>1148</td>
<td>1096</td>
<td>1698</td>
</tr>
<tr>
<td><strong>Ra</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca 0 ¹</td>
<td>4.5</td>
<td>524</td>
<td>812</td>
<td>741</td>
<td>1445</td>
</tr>
<tr>
<td>Ca 4</td>
<td>5.0</td>
<td>707</td>
<td>1000</td>
<td>1000</td>
<td>1621</td>
</tr>
<tr>
<td>Ca 8</td>
<td>5.4</td>
<td>851</td>
<td>1174</td>
<td>1258</td>
<td>1949</td>
</tr>
<tr>
<td>Ses 20 ²</td>
<td>4.7</td>
<td>562</td>
<td>954</td>
<td>812</td>
<td>1513</td>
</tr>
<tr>
<td>Ses 40</td>
<td>4.8</td>
<td>707</td>
<td>831</td>
<td>977</td>
<td>1621</td>
</tr>
<tr>
<td>Ses 80</td>
<td>5.3</td>
<td>794</td>
<td>954</td>
<td>1318</td>
<td>1621</td>
</tr>
<tr>
<td>Pea 20 ²</td>
<td>5.0</td>
<td>691</td>
<td>1071</td>
<td>977</td>
<td>1698</td>
</tr>
<tr>
<td>Pea 40</td>
<td>5.2</td>
<td>776</td>
<td>1202</td>
<td>1174</td>
<td>1905</td>
</tr>
<tr>
<td>Pea 80</td>
<td>5.6</td>
<td>933</td>
<td>1445</td>
<td>1258</td>
<td>2137</td>
</tr>
</tbody>
</table>

¹ Application rates of CaCO₃: 0, 4, 8 Mg ha⁻¹

² Application rates of sesbania and pigeon pea: 0, 20, 40, 80 Mg ha⁻¹
and Na (101 - 400 \(\mu M\)) were observed.

### 8.4.2 Effects of CaCO$_3$ and green manure amendments on rice growth

Plant height, dry weights, Al and Fe concentrations of shoots and roots, and relative root length at the time of harvest were used to measure rice response to the treatments (Table 8.6). Regression analysis of these growth parameters with activity of ions in the soil solution and plant nutrient compositions was performed (Table 8.7).

**Plant height.** The height of 60-d-old rice plants was drastically increased when either CaCO$_3$ or green manure treatments was applied (Table 8.6). In the unamended soils, the plant height were 73.0 - 74.4 cm and plant tops were stunted similar to those described by Foy (1974). In contrast, plant height was substantially increased to 77.6 - 85.7 cm by the addition of sesbania or pigeon pea at 20 Mg ha$^{-1}$. Applications of 40 or 80 Mg ha$^{-1}$ of the green manures appeared to be sufficient to suppress the harmful effects of Al, and produced the tallest plants (88.2 - 91.7 cm).

**Dry weights of shoots and roots.** Shoot dry weight increased with increasing rates of added CaCO$_3$ and green manures (Table 8.6). However, lime applications of 8 Mg CaCO$_3$ ha$^{-1}$ yielded lower dry matter (3.3 - 4.5 g pot$^{-1}$) than did the addition of 80 Mg ha$^{-1}$ pigeon pea. It is worth noting that the maximum yield (3.4 g pot$^{-1}$) was obtained at pH 5.4 in the Bg soil and at pH 5.6 in the Ra soil (4.8 g pot$^{-1}$). It is likely that the
Table 8.6. Plant height, dry weights, Al and Fe concentrations in shoots and roots, and relative root length of rice plants as affected by various levels of CaCO$_3$ (Ca), sesbania (Ses) and pigeon pea (Pea) application to two acid sulfate soils.

<table>
<thead>
<tr>
<th>Soils/ Treatments</th>
<th>Plant height (cm)</th>
<th>Dry weight shoots g pot$^{-1}$</th>
<th>Al conc. shoots mg kg$^{-1}$</th>
<th>Fe conc. shoots mg kg$^{-1}$</th>
<th>Relative root length $^\dagger$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bg</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca 0 $^\dagger$</td>
<td>73.0</td>
<td>2.09</td>
<td>0.41</td>
<td>749</td>
<td>5271</td>
</tr>
<tr>
<td>Ca 4</td>
<td>81.5</td>
<td>2.82</td>
<td>0.50</td>
<td>614</td>
<td>4272</td>
</tr>
<tr>
<td>Ca 8</td>
<td>91.0</td>
<td>3.39</td>
<td>0.76</td>
<td>525</td>
<td>3542</td>
</tr>
<tr>
<td>Ses 20 $^\ddagger$</td>
<td>78.6</td>
<td>2.55</td>
<td>0.46</td>
<td>695</td>
<td>4975</td>
</tr>
<tr>
<td>Ses 40</td>
<td>84.4</td>
<td>2.75</td>
<td>0.57</td>
<td>652</td>
<td>4448</td>
</tr>
<tr>
<td>Ses 80</td>
<td>90.8</td>
<td>3.01</td>
<td>0.60</td>
<td>576</td>
<td>4056</td>
</tr>
<tr>
<td>Pea 20 $^\ddagger$</td>
<td>81.1</td>
<td>2.86</td>
<td>0.60</td>
<td>613</td>
<td>4131</td>
</tr>
<tr>
<td>Pea 40</td>
<td>91.0</td>
<td>3.28</td>
<td>0.74</td>
<td>590</td>
<td>4068</td>
</tr>
<tr>
<td>Pea 80</td>
<td>88.8</td>
<td>3.49</td>
<td>0.80</td>
<td>481</td>
<td>3218</td>
</tr>
<tr>
<td>LSD$_{0.05}$</td>
<td>4.5</td>
<td>0.27</td>
<td>0.10</td>
<td>35</td>
<td>351</td>
</tr>
<tr>
<td>Ra</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca 0 $^\dagger$</td>
<td>74.4</td>
<td>3.04</td>
<td>0.71</td>
<td>473</td>
<td>4237</td>
</tr>
<tr>
<td>Ca 4</td>
<td>84.1</td>
<td>3.87</td>
<td>1.00</td>
<td>387</td>
<td>3401</td>
</tr>
<tr>
<td>Ca 8</td>
<td>90.5</td>
<td>4.50</td>
<td>1.41</td>
<td>337</td>
<td>2752</td>
</tr>
<tr>
<td>Ses 20</td>
<td>77.6</td>
<td>3.33</td>
<td>0.83</td>
<td>431</td>
<td>3871</td>
</tr>
<tr>
<td>Ses 40</td>
<td>89.5</td>
<td>3.64</td>
<td>1.07</td>
<td>416</td>
<td>3580</td>
</tr>
<tr>
<td>Ses 80</td>
<td>88.2</td>
<td>4.58</td>
<td>1.21</td>
<td>354</td>
<td>3013</td>
</tr>
<tr>
<td>Pea 20</td>
<td>85.7</td>
<td>4.22</td>
<td>1.12</td>
<td>396</td>
<td>3412</td>
</tr>
<tr>
<td>Pea 40</td>
<td>91.7</td>
<td>4.59</td>
<td>1.30</td>
<td>364</td>
<td>3114</td>
</tr>
<tr>
<td>Pea 80</td>
<td>88.8</td>
<td>4.87</td>
<td>1.49</td>
<td>304</td>
<td>2506</td>
</tr>
<tr>
<td>LSD$_{0.05}$</td>
<td>4.7</td>
<td>0.32</td>
<td>0.13</td>
<td>26</td>
<td>298</td>
</tr>
</tbody>
</table>

$^\dagger$ Application rates of CaCO$_3$: 0, 4, 8 Mg ha$^{-1}$

$^\ddagger$ Application rates of sesbania and pigeon pea: 0, 20, 40, 80 Mg ha$^{-1}$

$^\ddagger$ Data are average of three replications; the individual longest length was assigned to 100 %
Table 8.7. Relationship between growth parameters of rice plants and various Al toxicity indices derived from soil solution attributes in two acid sulfate soils (all treatments combined).

<table>
<thead>
<tr>
<th>Parameter and indices †</th>
<th>Regression equation ‡</th>
<th>r² §</th>
<th>Al 90% max. root length (μM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rel. dry weight of shoots vs. (Al³⁺)</td>
<td>Y = 74.4exp(0.01X)</td>
<td>0.82&quot;</td>
<td>-</td>
</tr>
<tr>
<td>Rel. dry weight of shoots vs. (AlSO₄²⁻)</td>
<td>Y = 76.3exp(0.009X)</td>
<td>0.89&quot;</td>
<td>-</td>
</tr>
<tr>
<td>Rel. dry weight of shoots vs. (SO₄²⁻)</td>
<td>Y = 0.8 + 0.03X</td>
<td>0.67&quot;</td>
<td>-</td>
</tr>
<tr>
<td>Rel. plant height vs. (Al³⁺)</td>
<td>Y = 89.2exp(0.003X)</td>
<td>0.72&quot;</td>
<td>-</td>
</tr>
<tr>
<td>Rel. plant height vs. (SO₄²⁻)</td>
<td>Y = 51.2 + 0.01X</td>
<td>0.48&quot;</td>
<td>-</td>
</tr>
<tr>
<td>Rel. plant height vs. (AlSO₄⁺)</td>
<td>Y = 90.1exp(0.005X)</td>
<td>0.76&quot;</td>
<td>-</td>
</tr>
<tr>
<td>Rel. root length vs. (SO₄²⁻)</td>
<td>Y = 37.8 + 0.02X</td>
<td>0.47&quot;</td>
<td>-</td>
</tr>
<tr>
<td>Rel. root length vs. (Al³⁺)</td>
<td>Y = 91.5 - 0.49X</td>
<td>0.67&quot;</td>
<td>3.0</td>
</tr>
<tr>
<td>Rel. root length vs. (AlSO₄⁺)</td>
<td>Y = 92.4 - 0.27X</td>
<td>0.64&quot;</td>
<td>8.6</td>
</tr>
<tr>
<td>Rel. root length vs. (Al₃⁺)</td>
<td>Y = 103.5 - 0.19X</td>
<td>0.50&quot;</td>
<td>70.0</td>
</tr>
</tbody>
</table>

† ( ) = activity in μM
‡ Y = Growth parameters; X = index
§ ** Significant at p < 0.01

most favorable growth conditions had not been attained in either soil by adding 8 Mg ha⁻¹ CaCO₃ or 80 Mg ha⁻¹ green manures.

CaCO₃ and green manure treatments had similar but less pronounced effects on roots than shoots (Table 8.6). Generally, additions of sesbania or pigeon pea green manure appeared to reduce Al toxicity in these acid sulfate soils. As mentioned previously, green manure treatments decreased
soluble Al with respect to the unamended treatments, suggesting Al precipitation/adsorption. Furthermore, shoot dry weights in the green manure treatments at 80 Mg ha\(^{-1}\) were either similar to or higher than those of CaCO\(_3\) treatments (8 Mg ha\(^{-1}\)) in both soils. It is possible that besides the pH effect on soluble Al, the forms of soluble Al and their corresponding phytotoxicity might be different among the treatments. In fact, many studies have demonstrated that low-molecular weight organic acids obtained from decomposition of organic materials can form non-toxic Al species by complexation (Bartlett and Riego, 1972; Hue et al., 1986).

**Aluminum concentration in shoots and roots.** Concentration of shoot Al was significantly affected by the treatments (Table 8.6). In general, CaCO\(_3\) application at 4 Mg ha\(^{-1}\) reduced shoot Al to 387.0 mg kg\(^{-1}\) in the Ra soil and 614.5 mg kg\(^{-1}\) in the Bg soil. The higher rate of 8 Mg ha\(^{-1}\) further reduced shoot Al to 337.9 and 525.3 mg kg\(^{-1}\) in the Ra and Bg soils, respectively. The green manure treatments of 80 Mg ha\(^{-1}\) also decreased shoot Al to 304.6 mg kg\(^{-1}\).

Like shoot Al, root Al also decreased with CaCO\(_3\) and green manure applications. Note that root Al was always 6 to 11 times higher than that in shoots. This is because Al is known to accumulate in roots of Al-tolerate plants, such as upland rice and cassava (Fageria et al., 1991).

**Relative root length (RRL).** Relative root length of rice plants after 60-day growth was increased with CaCO\(_3\) or green
manure applications (Fig. 8.2). The relative root length was calculated as the percentage of the individual longest root in each soil.

**Figure 8.2.** Effects of CaCO₃ (a), sesbania (b) and pigeon pea (c) application on relative root length of rice plants at 60 days after planting.

The 4 Mg ha⁻¹ CaCO₃ treatment resulted in similar values of RRL (84 and 85%) for both soils, which were significantly lower than the RRL (90%) at 8 Mg ha⁻¹ CaCO₃ but much higher than those of the unlimed control (Fig. 8.2). The results clearly
clearly demonstrated the beneficial effects of liming to rice growth on acid sulfate soils.

The sesbania treatment at 20 Mg ha\(^{-1}\) had no significant effects on RRL, especially in the Bg soil. Higher rates increased RRL, however. In contrast, the RRL in both soils increased with increasing pigeon pea additions up to 40 Mg ha\(^{-1}\), beyond that rate, RRL leveled off (Table 8.6).

8.4.3 Relationship between rice growth and soil-solution composition

Table 8.7 summarizes the correlations of plant growth with various soil solution parameters. The relationships between the growth parameters and the various indices of soluble Al are shown in Fig 8.3; all treatments in both soils were combined. The relation in Fig. 8.3a, indicates that relative plant height is positively correlated with soil solution pH \((r^2 = 0.63^{**})\), suggesting that rice plants were affected by soil acidity. A 10% reduction in relative plant height occurred at pH 4.8, implying that rice plants are moderately tolerant of acidity as previously noted by Blarney et al. (1987). Relative plant height was also negatively correlated with Al\(_{\text{sum}}\) activity \((r^2 = 0.60^{**}; \text{Fig. 8.3b})\).

Strong relationships were obtained between relative root length and Al\(^{3+}\), Al(SO\(_4\))\(^{3-}\) activities in a similar experiment reported by Bruce et al. (1988). The Al\(^{3+}\) activity corresponding to 80% RRL was 20 \(\mu M\). At 40 \(\mu M\) Al\(^{3+}\) activity, the RRL was reduced to 62% (Fig. 8.3c). An Al(SO\(_4\))\(^{3-}\) activity
Figure 8.3. Relationship between relative growth and soil solution composition of two acid sulfate soils.

of 30 µM reduced the RRL of rice plants by 20%. Perhaps, Al(SO₄)²⁺ is less toxic than Al³⁺ as suggested by Cameron et al. (1986). Thus, both Al³⁺ and Al(SO₄)²⁺ activities seem to be good indicators of Al toxicity for rice plants grown in acid sulfate soils. The critical value of 3.0 µM of Al³⁺ activity (Table 8.7) was in the same order of magnitude as 4 µM for upland rice root growth reported by Fageria et al. (1987).

Relative root length and relative dry weight of shoots were negatively correlated with Al_sum activity. When the Al_sum activity was ≥ 76.9 µM, the relative root length was ≤ 90%.
Thus $Al_{num}$ can also be used as an index of Al toxicity. However, the $Al_{num}$ index provided a lower $r^2$ value than that of $Al^{+3}$ activity (Table 8.7).

There was a strong correlation between RRL and Al and Fe in roots (Fig. 8.4). A 10% reduction in RRL occurred when root Al was 0.32% (Fig. 8.4a) or when root Fe was 0.29% (Fig. 8.4b).

![Graph a](image)

\[ Y^a = 117.6 - 0.008X \]
\[ r^2 = 0.51^{**} \]

![Graph b](image)

\[ Y^b = 117.3 - 0.009X \]
\[ r^2 = 0.49^{**} \]

**Figure 8.4.** Relationship between relative root length and Al or Fe concentration in rice roots.

Nutrient concentrations in rice plants were plotted against corresponding ionic activities in the soil solutions. Shoot K, Ca, Mg and S increased linearly with their corresponding
nutrients in the soil solution (Fig. 8.5a-d). All nutrients were very high in the soils after they were amended with CaCO₃ or green manures. Therefore, these nutrients were regarded as sufficient for rice growth.

![Graphs showing the relationship between K, Ca, Mg, and S concentrations in rice shoots and their respective activities in soil solution.]

**Figure 8.5.** Relationship between K, Ca, Mg, and S concentrations in rice shoots and their respective activities in soil solution.
8.5 Summary and conclusions

Acid sulfate soils in the Bangkok Plain of Thailand can be amended with either lime or green manures to grow upland rice. Sesbania and pigeon pea green manures at 40 Mg ha\(^{-1}\) were quite effective in Al detoxification of acid sulfate soils. Decreases in soluble Al as a result of CaCO\(_3\) or green manure amendments were probably responsible for better rice growth. The reduction in soluble Al was more pronounced in the pigeon pea treatments than in the sesbania treatments.

Plant height, shoot and root dry weight, and relative root length were good growth parameters in acid sulfate soils. Soil solution pH, and activities of Al\(^{3+}\), Al(\(\text{SO}_4\))^\(^+\) and Al\(_{\text{sum}}\) are among the soil-solution parameters which can be used to predict Al toxicity. Rice plants are also moderately tolerant to Al toxicity and grow well at pH ≥ 4.8, with Al\(^{3+}\) and Al\(_{\text{sum}}\) activities ≤ 3.0 and ≤ 70.0 \(\mu\)M, respectively.

A 90% maximum RRL is attainable when soil-solution Al\(^{3+}\) activity ≤ 10 \(\mu\)M, which is achievable by applying 44.4 Mg ha\(^{-1}\) of pigeon pea or 57.5 Mg ha\(^{-1}\) of sesbania, or 5.3 Mg ha\(^{-1}\) of CaCO\(_3\).
References


CHAPTER 9

Mineralogical and chemical properties of two acid sulfate soils as affected by lime and green manure application

9.1 Abstract

An incubation study was conducted to quantify the effects of lime or green manure on chemical and mineralogical properties of two acid sulfate soils from Thailand. The soils were a potential acid sulfate soil (Bg series; Typic Sulfaquents) and an actual acid sulfate soil (Ra series; Sulfic Tropaquepts); lime rate was 6 Mg ha\(^{-1}\) CaCO\(_3\); and sesbania green manure, 40 Mg ha\(^{-1}\). The temporal changes in chemical and mineralogical compositions of the soils were determined at 2, 14, 42 and 90 days after incubation. In the unamended soils, strong and rapid acidification occurred, resulting in pH decreases to 2.8 - 3.2. By contrast, liming and green manuring increased soil pH, EC, total exchangeable bases, and reduced Al saturation percentage. The reduction in Al was assumed to be the precipitation of soluble Al from pH increases resulted from lime or green manure addition.

X-ray diffraction analysis, on the other hand, showed no detectable change in clay minerals by either amendment, in spite of strong acidification occurring in the control. Detailed mineralogical study of handpicked yellow particles from soils 90 days after incubation showed the presence of
jarosite. Soil solution analysis suggested that jarosite might be formed by precipitation of K⁺, Fe³⁺ and SO₄²⁻.

Based on the ion activity product (pIAP) and stability diagram, Al-hydroxy sulfate minerals existed in the acid sulfate soils. The Al³⁺ activities were pH dependent and apparently controlled by the solubility of an alunite-like mineral having a pK_{sp} of 81.4.

9.2 Introduction

Acid sulfate soils are developed from the oxidation of pyrite (FeS₂) on exposure to the atmosphere due to drainage or crop cultivation. When the water table drops, oxygen enters the soil system and oxidizes pyrite by the following process (van Breemen, 1976):

\[ 2\text{FeS}_2 + 2\text{H}_2\text{O} + \text{O}_2 \rightarrow 2\text{Fe}^{2+} + 4\text{H}^+ + 4\text{SO}_4^{2-} \quad [1] \]
\[ 4\text{Fe}^{2+} + 10\text{H}_2\text{O} + \text{O}_2 \rightarrow 4\text{Fe(OH)}_3 + 8\text{H}^+ \quad [2] \]

The initial products are ferrous, sulfate and hydrogen ions; further hydrogen ions are released by the hydrolysis of ferrous iron and the precipitation of ferric oxide. Under acid conditions, ferric ions can also oxidize pyrite:

\[ \text{FeS}_2 + 14\text{Fe}^{3+} + 8\text{H}_2\text{O} \rightarrow 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+ \quad [3] \]

The oxidation of ferrous to ferric is catalyzed by the bacterium *Thiobacillus ferrooxidans* under acid conditions. Oxidation of pyrite by this route is nearly \(10^6\) times faster than reactions [1] and [2] (Ritsema et al. 1992).
Acid sulfate soils are characterized by a low pH and the presence of yellowish jarosite \((\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6)\) mottles in the soil profile at various depths. According to van Breemen (1982), jarosite is usually found under conditions of low pH (2 - 4) and strongly oxidizing environments \((\text{Eh} > 400 \text{ mV})\). Incomplete hydrolysis of ferric iron can also produce jarosite, and acidity \((\text{H}^+)\):

\[
\text{FeS}_2 + 15/4\text{O}_2 + 5\text{H}_2\text{O} + 1/3\text{K}^+ \rightarrow 1/3\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6 + 4/3\text{SO}_4^{2-} + 3\text{H}^+ \quad [4]
\]

Besides jarosite and/or natrojarosite, Al-hydroxy sulfate minerals such as alunite \((\text{KAl}_3(\text{OH})_6(\text{SO}_4)_2)\), jurbanite \((\text{AlOHSO}_4)\), and basaluminite \((\text{Al}_4(\text{OH})_10\text{SO}_4)\) can also be found in acid sulfate soils. Low pH and high \(\text{Al}^{3+}, \text{Fe}^{3+}, \text{SO}_4^{2-}\), and \(\text{K}^+\) activities favor the formation of these minerals.

Under a scanning electron microscope, jarosite appears as cubes occupying voids and/or root channels. It has been suggested that jarosite is formed by pseudomorphic replacement of pyrite (Shamshuddin et al., 1986). Mermut et al. (1985) however, questioned this mechanism in soil as pyrite crystals were far too big compared to jarosite crystals.

Some acid sulfate soils in the Bangkok Plain have been reclaimed for paddy rice, tropical fruit trees and upland crops (Panichapong, 1990). The routine management and agronomic practices for traditional rice production on these soils consist of 1) leaching and flushing the excess acidity by rain water and flood-swollen stream water, 2) liming and/or 3) incorporating rice straw or organic residues into the top
soil. Liming has been practiced on rice fields, but the practice is not effective in acid sulfate soils because large amounts of lime are required. For clay-textured acid sulfate soils, repeated applications of 20 Mg of CaCO$_3$ ha$^{-1}$ year$^{-1}$ (Moore et al. 1990) are common. Hence, alternative practice using organic amendments to reduce or prevent Al toxicity in the rice fields is worth investigating. Some green manure, crop residue, chicken manure and sewage sludge have been shown to decrease Al toxicity in acid soils (Hue and Amien, 1989; Hue, 1992). The possible reactions include chelation of Al$^{3+}$ by functional groups on the solid phase of organic amendments or by the soluble organic components. The objectives of this study were to assess chemical and mineralogical changes in some acid sulfate soils of Thailand as a consequence of lime and green manure applications.

9.3 Materials and methods

9.3.1 Soil selection and properties

Two soils from the Bangkok Plain, one at the Bang Pakong Soil Conservation Center in the Chachoengsao Province, and the other from the Ongkharak Acid Sulfate Soil Experiment Station in the Nakhon Nayok Province, were selected for the study. The soils belonged to the Bang Pakong (Bg) and Rangsit-very acid phase (Ra) series.

The Bg soil is classified as a Typic Sulfaquent (Soil Survey Staff, 1990), which was under mangroves that have been
cleared for rice production. The soil is subjected to salt water intrusion at high tide during dry seasons. It is protected from saltwater intrusion by local farmers for rice cultivation during the wet season after the first rain waters have flushed surface salts that accumulated during the previous dry season. During our 1992 investigation, this area was undergoing intense reclamation/management practices. The area was being drained by the construction of a deep canal and protected from sea water by a seawall dam. This soil was selected to represent the potential acid sulfate soils.

The Ra soil is classified as a Sulfic Tropaquept (Soil Survey Staff, 1990). This soil has been drained and leached by rain water since 1970. The soil had been planted to continuous rice for 15 years. Fresh water was used to irrigate rice during the dry season. Lime, N and P had been used during rice production. This soil was selected to represent the actual acid sulfate soils.

Soil samples, about 60 kgs from each series, were collected from the Ap horizons and jarositic layers. The samples were air-dried, ground, sieved through a 2-mm screen, and shipped to the Department of Agronomy and Soil Science, University of Hawaii, for an incubation study.

9.3.2 Chemical analysis

Soil samples were analyzed for texture and relevant chemical constituents. Soil pH was measured on previously air-
dried samples suspended in a 1:1 soil : water. Soil electrical conductivity (EC) of 1:1 soil : water ratio was obtained by a conductivity bridge. Extractable bases were determined in the 1M NH₄OAc extract, buffered at pH 7. Calcium and Mg were measured by atomic absorption spectrophotometry (AAS), while Na and K were determined by flame photometry. Aluminum was extracted by 1M KCl and determined colorimetrically (Barnhisel and Bertsch, 1982). The acid-oxalate method of McKeague and Day (1966) was used to extract amorphous Fe and Al oxides. Oxalate-Fe in the extracts was analyzed by AAS. Oxalate-Al was determined colorimetrically by the catechol violet procedure (Kerven et al., 1989).

9.3.3 Mineralogical analysis

Particle size segregation. Mineral analysis was carried out on air-dried, sieved (< 2 mm) soil samples, which were first subjected to ultrasonic dispersion and centrifugation to obtain different particle size classes. The clay fraction (< 2 μm) was further separated into coarse (2 - 0.2 μm) and fine (< 0.2 μm) fraction. Only X-ray diffraction patterns of the coarse clay fraction will be presented and discussed in this paper.

X-ray diffraction (XRD). Inasmuch as the clay fraction cracked and curled when placed on a glass slide, the clay was air dried, ground with a mortar and packed into cavity mounts. The samples were, therefore, randomly oriented and as much produced diffraction lines that were proportional to the
actual amounts of the minerals present. Random orientation, however, does not accentuate the basal reflections of the phyllosilicates. In addition, the untreated soil samples containing yellow mottles at 90 days after incubation were handpicked and analyzed by XRD. XRD was carried out with a Philips Norelco diffractometer with a long fine-focus cobalt target X-ray tube operated at 40 kV, 25 mA. A curved graphite monochrometer was used in place of a Kβ filter. XRD intensities were collected by step scanning the specimens from 4° to 76° 2θ with a step size of 0.025° 2θ and with a 4 sec counting time per step. Data were collected by a computer and stored on disks for further processing.

9.3.4 Soil incubation study

An incubation experiment was conducted, using a split-plot design with incubation periods as main plots and soil amendments as subplots. Each treatment was duplicated. The amendments were: control (no addition); 6 Mg CaCO₃ ha⁻¹ (3.0 g kg⁻¹ soil, the nominal lime requirement); and 40 Mg ha⁻¹ grounded sesbania tops (20 g kg⁻¹ soil). These rates were chosen based on the results of previous experiments (Chapter 8). The CaCO₃ or sesbania tops (containing in % of dry matter: 3.20 N; 0.25 P; 2.12 K; 0.94 Ca and 0.93 Mg) were incubated with 300 g air-dried soils in thin (0.025 mm) polyethylene bags at 24 ± 1 °C. The soils, CaCO₃ or sesbania amendments were well mixed before being brought to 80% of the field water holding capacity with deionized water. The incubation bags
were not sealed but folded over to allow adequate aeration. Any water loss, which was less than 3% per week, was replaced weekly. The amended soils were sampled at 2, 14, 42 and 90 days after incubation, and the soil solution was extracted.

**Soil solution collection and chemical speciation.** The soil samples from each treatment were rewetted with deionized water to field capacity and equilibrated for 1 day. Then the soil solution was extracted by centrifugation (Menzies and Bell, 1988). The solution was filtered through a 0.45 μm-pore membrane. The pH and EC were determined immediately on 3 mL subsamples. The remaining soil solution was kept for chemical analyses. Calcium, Mg, K, Na, Fe and Mn were determined by atomic absorption spectrophotometry; NO₃⁻ by the phenoldisulfonic acid method (Hue and Evans, 1986), P by the ammonium sulfomolybdate method (Olsen and Sommers, 1982), SO₄²⁻ by the turbidimetric method (Freeney, 1986), and dissolved organic C by the pyrophosphate-Mn³⁺ method of Bartlett and Ross (1988). The catechol violet method as described by Kerven et al. (1989) was used to determine the total inorganic Al concentration in soil solution.

Activities of Al species and other ions in the soil solutions were calculated by the SOILSOLN computer program of Wolt (1987). Soil solution pH, and concentrations of Al, Ca, Mg, Na, K, Mn, P, NO₃⁻, SO₄²⁻ and soluble organic C were used as input. Ionic strength of the soil solution was estimated from the EC (Griffin and Jurinak, 1973). Inorganic monomeric Al
species in soil solution considered are \( \text{Al}^{3+}, \text{Al}(	ext{OH})^{2+}, \text{Al}(	ext{OH})_2^+, \text{Al}(	ext{OH})_3^0 \) and \( \text{Al}(	ext{SO}_4)^+ \) (Blamey et al., 1983). The sum of the activities of these Al species is termed \( \text{Al}_{\text{sum}} \).

Ion activities in soil solution were used to construct ion activity products (IAP) and mineral stability diagrams. Stability lines for various minerals were drawn based on the information reported by Lindsay (1979), and Garrels and Christ (1965).

9.3.5 Statistical analysis

The main effects of incubation periods and comparisons among treatments were statistically analyzed following the split-plot design. Analysis of variance was performed and the level of significance was set at 5% (\( p < 0.05 \)) unless otherwise specified.

9.4 Results and discussion

9.4.1 Effects of CaCO\(_3\) and green manure on the soil solid phase

Effects of the amendments on soil pH (1:1), EC, exchangeable and Al saturation percentage of the effective CEC of the soils at various incubation periods are shown in Table 9.1. In general, significant changes (\( p < 0.05 \)) in some soil-solid phase properties were observed by effects of time of incubation and interaction of the incubation periods with soil amendments in pH, EC, and Al saturation percentage. The trends were similar for all two acid sulfate soils and are
Table 9.1. Chemical properties of the soil solid phase as affected by CaCO$_3$ (6 Mg ha$^{-1}$) and sesbania (40 Mg ha$^{-1}$) application at various incubation periods for two acid sulfate soils.

<table>
<thead>
<tr>
<th>Treatments</th>
<th>Incubation period (days)</th>
<th>pH</th>
<th>EC (dS m$^{-1}$)</th>
<th>Ex.AI</th>
<th>ECEC $^+$ (cmol$_e$ kg$^{-1}$)</th>
<th>Al sat. (%)</th>
<th>Ca sat. (%)</th>
<th>Al$_{out}$$^v$ (%)</th>
<th>Fe$_{out}$$^v$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>6.4</td>
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<td>8.2</td>
<td>44.7</td>
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<tr>
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<td>47.6</td>
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<td>0.7</td>
<td>3.1</td>
<td>1.7</td>
<td>0.02</td>
<td>0.03</td>
</tr>
</tbody>
</table>

$^+$ ECEC = Total exchangeable bases + Total exchange acidity

$^v$ extracted with 0.2 M Ammonium oxalate (pH 3.0)

$^v$ LSD (0.05) values for differences among treatments
illustrated in Table 9.2 using the statistically significant values of F-test of analysis of variance (ANOVA). The soils were very acid with the initial pH ranging from 3.5 - 3.6. Within 90 days of incubation, the pH levels dropped significantly (P < 0.01) in the unamended soils. Strong acidification was probably caused by the formation of H₂SO₄ due to the oxidation of pyrite and ferrous sulfide (van Breemen, 1976). Acidification was extreme in the Bg soil (pH = 2.8) and relatively moderate in the Ra soil (pH = 3.2).

Table 9.2. Summary of source, degree of freedom (df) and F-value of analysis of variance for soil-solid phase as affected by CaCO₃ (6 Mg ha⁻¹) and sesbania (40 Mg ha⁻¹) application at various incubation periods for two acid sulfate soils.

<table>
<thead>
<tr>
<th>Source</th>
<th>df</th>
<th>F-value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>pH (1:1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EC (dS m⁻¹)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ex.Al (cmol, kg⁻¹)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Al sat. (%)</td>
</tr>
<tr>
<td>Bang Pakong (Bg)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Block</td>
<td>1</td>
<td>2.46 NS</td>
</tr>
<tr>
<td>Incubation (I)</td>
<td>3</td>
<td>3.92 NS</td>
</tr>
<tr>
<td>Error (a)</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Treatment (T)</td>
<td>2</td>
<td>88.83 **</td>
</tr>
<tr>
<td>IxT</td>
<td>6</td>
<td>7.78 *</td>
</tr>
<tr>
<td>Error (b)</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>Rangsit (Ra)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Block</td>
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<td>3.54 NS</td>
</tr>
<tr>
<td>Incubation (I)</td>
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<td>4.23 NS</td>
</tr>
<tr>
<td>Error (a)</td>
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<td></td>
</tr>
<tr>
<td>Treatment (T)</td>
<td>2</td>
<td>108.29 **</td>
</tr>
<tr>
<td>IxT</td>
<td>6</td>
<td>9.84 **</td>
</tr>
<tr>
<td>Error (b)</td>
<td>8</td>
<td></td>
</tr>
</tbody>
</table>

1 NS: Nonsignificant; * **: Significant at the 0.05 and 0.01 % level, respectively.
As expected, soil pH and EC increased with CaCO₃ or sesbania addition. The application of either amendment increased soil pH by about 0.8 - 0.9 units in the Bg soil and by about 1.1 - 1.3 units in the Ra soil after 90 days of incubation. Accordingly, KCl-extractable Al was decreased from 6.4 cmolₑ kg⁻¹ to 0.4 cmolₑ kg⁻¹ in the Bg soil and from 4.0 cmolₑ kg⁻¹ to 0.1 cmolₑ kg⁻¹ in the Ra soil.

Aluminum saturation value of the unamended soils always exceeded 40%, regardless of the incubation periods (Table 9.1). Such levels have been reported to adversely affect crops grown in the Bangkok Plain (Osborne, 1985). Adding CaCO₃ or sesbania green manure gradually decreased Al saturation which declined to less than 10% after 90 days of incubation.

Exchangeable bases increased significantly with liming and sesbania amendments, and also with incubation time. Calcium was low in both unamended soils where Ca saturation percentage of the effective CEC was 5.1% and 8.7% (Table 9.1). These Ca saturation values are much less than the reported values of 12% - 13% below which cotton root penetration into acid Ultisols of Alabama was restricted (Howard and Adams, 1965). Ca saturation increased with CaCO₃ addition for each incubation period. The significant increase (43.2 - 61.3%) occurred in Ra soil. Liming acid sulfate soils with CaCO₃ may take considerable time to be effective. The one- or two-week waiting period between liming and planting, as recommended for "regular" acid soils, may not be adequate for acid sulfate
soils. Addition of 40 Mg ha\(^{-1}\) sesbania to both soils also increased Ca saturation above 12.7 - 19.9% which is higher than 11% reportedly required for 90% relative root length of soybean (Bruce et al., 1988).

The oxalate-extractable Al and Fe contents varied considerably among the treatments and incubation periods. The acid-oxalate solution presumably extracts the amorphous Fe oxide and/or amorphous Al hydroxides and oxyhydroxides from the soils. The NH\(_4\) oxalate solution extracted more Al from the control than from the sesbania amended soils (1.54% vs. 1.30% in the Bg soil, and 0.69% vs. 0.30% in the Ra soil). Similarly, NH\(_4\) oxalate extracted 1.42% Fe in the unamended Bg soil and 1.12% Fe in the sesbania treatment after 90 days of incubation.

It is expected that microcrystalline Al oxides would form as a result of liming of acid sulfate soils. Raising soil pH by lime converts most of the exchangeable and some amorphous Al to Al oxides and hydroxides, which are not extracted by NH\(_4\) oxalate. Organic matter also forms solid complexes with amorphous Al (Greenland, 1971), making Al nonextracted by NH\(_4\) oxalate at extended periods of incubation.

9.4.2 Effects of CaCO\(_3\) and green manure on soil-solution phase

\(\text{pH, electrical conductivity and ionic strength (I)}\)

The effects of CaCO\(_3\) and sesbania treatments on soil solution pH, EC and ionic strength are summarized in Table
9.3. At 90 days after incubation, CaCO₃ application increased soil solution pH from 3.92 to 5.83 in the Bg series and from 4.35 to 5.92 in the Ra series. A highly significant increase in pH and EC with 40 Mg ha⁻¹ sesbania application was also observed in both soils. The pH was raised from 3.92 to 5.11 in the Bg soil, and from 4.35 to 5.86 in the Ra soil at 90-day incubation. By contrast, pH of the control soils decreased significantly from 3.92 to 3.49 in the Bg series, and varied slightly from 4.35 to 4.19 in the Ra series.

Soil-solution ionic strength of the unamended Bg soils was $< 20.1 \text{ mM}$ and decreased with incubation time, whereas the ionic strength increased from 29.9 - 44.2 mM after 90 days of incubation in the CaCO₃ treatment. In general, soil-solution ionic strength (I) was greater with CaCO₃ than with the sesbania treatment. For example, I was 41.2 mM in the Ra soil incubated with CaCO₃ and 34.4 mM incubated with sesbania.

**Basic cation concentrations**

Soil-solution K in the unamended soils was generally low, ranging from 202 - 301 μM depending on incubation period. For comparison, Edmeades et al. (1985) found a mean K concentration in the soil solution for a group of acidic top soils in New Zealand to be 640 μM (range 240 to 1030 μM). The lack of K-bearing minerals such as feldspar and secondary micaceous minerals, and the possible formation of sparingly soluble K bearing sulfate minerals in our acid sulfate soils can explain for such low K concentrations.
Table 9.3. pH, EC and cationic concentrations in the soil solution as affected by CaCO₃ (6 Mg ha⁻¹) and sesbania (40 Mg ha⁻¹) application at various incubation periods for two acid sulfate soils.

<table>
<thead>
<tr>
<th>Treatments/ Incubation periods (days)</th>
<th>pH</th>
<th>EC (dS m⁻¹)</th>
<th>I[^t] (mM)</th>
<th>Na</th>
<th>K</th>
<th>Ca</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bang Pakong (Bg)</td>
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<td></td>
<td></td>
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<td></td>
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<td></td>
</tr>
<tr>
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<td>1.5</td>
<td>20.1</td>
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<td>301</td>
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[^t] I (mM) = 13 * EC (dS m⁻¹)

[^v] LSD (0.05) values for differences among treatments
In general, all basic cations in the soil solution of the CaCO$_3$ treatment were at higher concentrations than those in the unamended soils after 90 days of incubation. Furthermore, the predominant cation in the soil solution of the unamended treatment was Na, whereas expectedly it was Ca in the CaCO$_3$ treatment. The common notion that Ca is the dominant cation in soil solutions does not apply to acid sulfate soils. The dominance of Na ions (in molar concentration terms) in soil solutions has been reported by Ahmad and Wilson (1992) and Cisse et al. (1993) for many acid sulfate soils in regions of the Caribbean and the Republic of Guinea. These investigators attributed the high Na concentrations in soil solution to the weak adsorption of Na on the exchange complex. High Na concentrations in our soils however, may also be related to the inundation of salt water during the dry season.

Compared with the CaCO$_3$ treatment, the application of sesbania green manure significantly increased the concentration of Ca and Mg in the soil solution at each incubation period. Between the two soils, soil-solution Ca concentration of the sesbania amended Ra series was higher than that of the Bg series (Table 9.3). For example, at 90 days of incubation the Ca concentration was 3211 $\mu$M in the Ra soil as compared to 2401 $\mu$M in the Bg soil. The increase in Mg concentration to 3706 $\mu$M in the Ra soil was also due partly to the addition of Mg from decomposing sesbania directly to the soil solution. Thus, green manure application helps improve
the availability of Ca and Mg, making these nutrients in acid sulfate soils more favorable for crop production.

There was no useful relationship found between basic cations in soil solution and exchangeable cations of the two acid sulfate soils. By contrast, Nemeth et al. (1970) observed a close relationship between exchangeable Ca and Ca in soil solution for a group of temperate soils. Edmeades et al. (1985) also found a positive relationship between concentrations of cations in soil solution and amounts of these nutrients present in exchangeable form. Although exchangeable cations are often used as indicators of soil fertility management, it may be inappropriate to emphasize such parameters in these acid sulfate soils.

**Total concentrations of soluble Al, Fe and Mn**

Due to the strongly acid nature and the continuous oxidation in both acid sulfate soils, water soluble Al, Fe and Mn in the unamended treatments increased significantly throughout the incubation periods. Concentrations of Fe were 54.8 - 112.4 \(\mu M\); Mn, 53.9 - 75.5 \(\mu M\); and Al, 111.4 - 238.7 \(\mu M\) (Table 9.4).

The high concentrations of Al and Mn in the soil solution are often regarded as the most limiting factors for crop production in acid sulfate soils. These Al and/or Mn toxicities can be alleviated by either CaCO\textsubscript{3} or sesbania application (Table 9.4). There was an exponential relationship
Table 9.4. Concentrations of Al, Fe, Mn and anions in the soil solution as affected by CaCO₃ (6 Mg ha⁻¹) and sesbania (40 Mg ha⁻¹) application at various incubation periods for two acid sulfate soils.

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⁷LSD (0.05) values for differences among treatments
between soil solution Al concentration and soil solution pH for all treatments of both soils (Figure 9.1a). When pH was raised to 5.0 after 90 days of incubation, Al concentration was reduced to less than 30 µM, a level considered as nontoxic.

**Figure 9.1.** Relationship between Al (a), Mn (b) and Fe (c) concentrations and pH in the soil solution of two acid sulfate soils. Regression equation for a). \( Y' = 2.5 \times 10^4 (\exp^{-1.2X}), r^2 = 0.92''; \) b). \( Y' = 164.0 - 25.6X, r^2 = 0.97''; \) and c). \( Y' = 193.8 - 29.7X, r^2 = 0.93''. \)
to most plants (Ismail et al., 1993). Similar results have been reported for acid sulfate soils from Malaysia (Edgardo and Shamshuddin, 1991) and Indonesia (Konsten et al., 1990).

There were also high linear correlations \( r^2 = 0.97** \), \( 0.93** \), respectively) between Mn or Fe concentration and pH (Fig. 9.1b and c). For example, when soil pH was raised to 5.11 in the Bg and 5.86 in the Ra soil by the green manure treatment, Mn concentration was decreased to 30 - 10 \( \mu M \), and Fe concentration to 40 - 15 \( \mu M \).

**Activities of Al species and basic cations**

Both CaCO\(_3\) and green manure application affected the calculated activities of Al, Mn, basic cations and \( SO_4^{2-} \) in the soil solution (Table 9.5). The production of \( SO_4^{2-} \) is clearly demonstrated after 90 days of incubation, which shows a rapid rise in \( SO_4^{2-} \) activities to values of around 4786 - 5370 \( \mu M \). In contrast to the increasing \( SO_4^{2-} \) activities, Mn activities decreased in the liming and sesbania treatments.

Along with exchangeable Al and/or Al saturation, Al activity in soil solution has been used to predict Al toxicity. The Al\(^{3+}\) and monomeric Al hydroxy species in solution are more toxic to plants than soluble polymeric species (Blamey et al., 1983). Adams and Lund (1966) observed a critical solution Al\(^{3+}\) activity of 2 \( \mu M \) for cotton roots. Using the derived equation of \( pAl^{3+} = 1.72pH - 2.22, r^2 = 0.94** \) from both acid sulfate soils, 2 \( \mu M \) Al\(^{3+}\) is attainable when soil solution pH \( \geq 4.6 \).
Table 9.5. Effects of CaCO₃ (6 Mg ha⁻¹) and sesbania (40 Mg ha⁻¹) application on pH and activities of ions in the soil solution at various incubation periods for two acid sulfate soils.

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</table>

¹ Alₜₜ = Al⁺³ + Al(OH)⁺² + Al(OH)₂⁺ + Al(OH)₃⁺ + Al(SO₄)⁺

Most of soil solution Al was in the inorganic monomeric form. The Al⁺³ activity in the unamended Bg and Ra soils was 26.3 and 12.2 µM, respectively. In the CaCO₃ treatment, Al⁺³ and AlSO₄⁻ dominated the Al species initially but their activities were...
reduced significantly as soil solution pH increased with incubation time (Table 9.5). In the sesbania treatments, Al$^{3+}$ activity in the soil solution was 0.8 μM in the Bg soil, and practically zero (< 0.1 μM) in the Ra soil after 90 days of incubation. The reduction in Al$^{3+}$ activity by green manure application has been reported by Hue and Amien (1989). Furthermore, high activities of K$^+$, SO$_4^{2-}$, and H$^+$ may result in a precipitation of Al-hydroxy sulfates (Hue et al., 1985), which reduces Al$^{3+}$ activity.

9.4.3 Mineralogical composition of acid sulfate soils

XRD analysis of the clay fraction

In general, there was no change in the X-ray diffraction patterns of the clay fractions of both acid sulfate soils by application of CaCO$_3$ or sesbania green manure during the 90-day incubation period (Fig. 9.2 and 9.3). The oriented clay prepared from the unamended Bg soil samples invariably showed distinct peaks at 7.15, 10.56 and 14.82 °A (Fig. 9.2), indicating the presence of kaolinite, illite and high-charge smectite, respectively. The Ra-soil samples had a similar clay mineralogy (Fig. 9.3), except that small peaks were found at 14.0 - 14.1 °A for all treatments at 90 days after incubation. For both acid sulfate soils, 2:1 type clay of smectitic peak appeared at 14.82 °A consistently throughout the incubation periods. Kaolinite (7.16 °A) was also evident in all samples. Kaolinite may be considered as a weathering
Figure 9.2. X-ray diffraction patterns of the clay fraction of the Bg soil as affected by CaCO$_3$ and sesbania application at 2 and 90 days after incubation. Ca 0 = Control; Ca 6 = 6 Mg ha$^{-1}$ CaCO$_3$; Ses 40 = 40 Mg ha$^{-1}$ sesbania.
Figure 9.3. X-ray diffraction patterns of the clay fraction of the Ra soil as affected by CaCO$_3$ and sesbania application at 2 and 90 days after incubation. Ca 0 = Control; Ca 6 = 6 Mg ha$^{-1}$ CaCO$_3$; Ses 40 = 40 Mg ha$^{-1}$ sesbania.
product of smectites (Bohn et al., 1985). The XRD analysis showed no evidence of weathering of clay minerals by the treatments in spite a strong acidification that occurred during the incubation in the control soils. The acidity produced from intense pyrite oxidation in the present study did not induce weathering of clay minerals. It is likely that an incubation of 90 days was too short for mineral weathering.

**XRD analysis of basic ferric sulfate minerals**

After 42 days of incubation, a few small straw yellow spots appeared on the upper surface of the unamended Bg soil. Later the spots became larger and turned pale yellow (2.5 - 5Y 8/3-8/6). These particles were handpicked at 90 days after incubation for X-ray analysis (Fig. 9.4). Jarosite was found to be the only basic ferric sulfate mineral present in the yellow mottles. Besides jarosite the remaining yellow mottles had peaks that were attributable to quartz, mica, feldspar and in one instance pyrite. Neither natrojarosite, ammonium-jarosite, hydronium jarosite, alunite, jurbanite, goethite nor hematite could be observed in this yellow mottle. Although the XRD patterns of the basic ferric sulfate minerals differed only slightly, the position of the (003) reflection at about 4.2 to 4.4 Å and the (021) and (113), double reflection at 3.1 Å, permitted the separation of jarosite from other basic ferric sulfate minerals. Under the present study jarosite was identified by its (003) reflection at 4.46 Å and its (021)
Figure 9.4. X-ray diffraction patterns of materials separated from yellow mottles from the Bg soil after 90 days of incubation. Only the distinct jarosite peak (at 3.18 Å) is shown with symbol J.

and (113) doublet at 3.18 and 3.07 Å, respectively. The 4.25 Å and 3.33 Å XRD peaks were the peaks of quartz, which were present together with the yellowish mottles.

The particles of the yellow mottle collected from the jarositic horizon in the field conditions of the Bg soil had
similar XRD pattern to that of jarosite; no natrojarosite and other minerals could be detected (data not shown). This was probably due to the fact that most Na was already leached from the soil when the jarositic layer began to form, and the formation of natrojarosite in situ is a slow process. The above results are in good agreement with synthetic and naturally occurring basic ferric sulfate. For example, in the formation of synthetic basic ferric sulfate (Ivarson et al., 1982), there was a strong preference for K⁺ over Na⁺ and H₃O⁺ in the structure. In a survey of acid sulfate soils (> 8000 km²) in the Bangkok Plain of Thailand, van Breemen (1976) showed that K-jarosite was far more abundant than the Na or H₃O-form. Our results also confirmed that there was a strong preference for the formation of jarosite after 90 days of incubation.

X-ray diffraction analysis, generally supported the contention that smectite, kaolinite, illite and jarosite are the four major minerals present in our acid sulfate soils. The presence of basic aluminum sulfate and/or Al hydroxy sulfate minerals (e.g., jurbanite, basaluminite and alunite) was not evident or detected by XRD. Apparently, their low concentrations and small crystallite size were not detectable by our X-ray equipment. Identification or verification of these minerals may require higher resolution instruments (SEM or electron micrographs) or other more effective techniques.
9.4.4 Effects of lime and green manure on metal solubility and mineral stability diagrams

Aluminum and Fe are two important metals in acid sulfate soils contributing to the dissolution, precipitation, and formation of various hydroxy-sulfate minerals. Among these, jarosite \((\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6)\) is one of the most important minerals in acid sulfate soils, and very insoluble with a \(K_{sp}\) value of \(10^{-38.6}\) (Vlek et al., 1974). Ion activity products (IAP) were calculated for jarosite with the SOILSOLN program. The results showed that the saturation indices \((\text{IAP}/K_{sp})\) were greater than zero, suggesting that our soil solutions were supersaturated with respect to jarosite. In other words, jarosite should be present or is being formed in our acid sulfate soils; and indeed the XRD data confirmed this.

When the soils were amended with 6 Mg ha\(^{-1}\) of CaCO\(_3\) or 40 Mg ha\(^{-1}\) of sesbania, soil solution pH increased above 5 after 90 days of incubation (Table 9.3). This condition is no longer conducive for jarosite formation, which requires low pH (2 - 4) and in an oxidizing environment (\(Eh > 400 \text{ mV}\)) (van Breemen, 1982).

**Ion activity products and mineral stability diagram**

The formation of Al-hydroxy sulfate minerals [jurbanite \((\text{AlOHSO}_4)\), basaluminite \((\text{Al}_4(\text{OH})_{10}\text{SO}_4)\), and alunite \((\text{KAl}_3(\text{OH})_6\text{SO}_4)\)] were studied by comparing ion activity and corresponding \(K_{sp}\) for each mineral. Table 9.6 shows the possibility of Al-hydroxy sulfate formation with respect to
Table 9.6. Soil solution ion activities and ion activity products of acid sulfate soils as affected by CaCO₃ (6 Mg ha⁻¹) and sesbania (40 Mg ha⁻¹) application at various incubation periods for two acid sulfate soils.

<table>
<thead>
<tr>
<th>Treatments/Incubation periods</th>
<th>pH</th>
<th>-log activity (mol L⁻¹)</th>
<th>Ion activity products</th>
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**Bang Pakong (Bg)**

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**Reference**

van Breemen, 1973; Adams and Rawajifih, 1977; Kittrick, 1966;
lime and sesbania amendments at various incubation periods. Since the overall ion activity products were $10^{-81.4}$ for alunite ($K_{sp} = 10^{-85.4}$) and $10^{-118.5}$ for basaluminite ($K_{sp} = 10^{-117.6}$), our soil solutions were generally oversaturated with respect to crystalline alunite, but undersaturated with respect to basaluminite. Eriksson (1993) suggested alunite formation as the solid phase immobilization of Al in the Me Kong acid sulfate soils of Vietnam under the different water managements. On the other hand, the existence of jurbanite seems to depend on the soil amendments. In the unamended controls, the soil solutions had $-\log$ (ion activity product) for jurbanite ($p_{Jurb.}$) of 17.3 ± 0.1 for the Bg soil and 17.2 ± 0.1 for the Ra soil, which are similar to the reported solubility range of jurbanite [$pK_{sp} = 17.2$ (van Breemen, 1973) or 17.8 (Nordstrom, 1982)]. As lime was added, and the incubation time was extended, the soil solution became undersaturated with respect to jurbanite and oversaturated with respect to alunite. It is possible that jurbanite was dissolving to form alunite upon $OH^-$ (lime) addition as suggested by the following reaction:

$$3Al(OH)SO_4 + 3OH^- + K^+ \rightarrow KAl_2(OH)_6(SO_4)_2 + SO_4^{2-}$$  \[5\]

For example, the limed Bg soil had $p_{Jurb.} = 17.2$ at 2-day incubation, which changed to 18.3 after 42 days of incubation. At the mean time, $p_{Alunite}$ fluctuated about 80.3 in the lime treatment as compared to 84.5 in the unamended control. Such shifts in ion activity products also occurred in the sesbania
green manure treatment as clearly demonstrated in the Ra soil. Changes due to green manure addition were more subtle because the Bg soil was too acid for fast organic decomposition.

Stability diagrams of the Al-hydroxy sulfate minerals were plotted in Fig. 9.5. Using reference $pK_{sp}$ of 17.2 for jurbanite (van Breemen, 1973), 117.6 for basaluminite (Adams and Rawajifih, 1977), 85.4 for alunite (Adams and Rawajifih, 1977), 32.8 for microcrystalline gibbsite (Kittrick, 1966), and 14 for water ($pK_w$), the following relationships are established (parentheses denote ion activities, brackets are used for grouping).

For jurbanite, $p(\text{Al}^{3+})(\text{OH}^-)(\text{SO}_4^{2-}) = [p\text{Al} + p\text{OH} + p\text{SO}_4] = 17.23$ \[6\]

For basaluminite, $p(\text{Al}^{3+})^4(\text{OH})^{10}(\text{SO}_4^{2-}) = 6pK_w$

$$= 4[p\text{Al} + p\text{OH} + p\text{SO}_4] - 3[2p\text{H} + p\text{SO}_4]$$

$$= 33.6$$ \[7\]

which, on rearrangement, yields

$$[p\text{Al} + p\text{OH} + p\text{SO}_4] = 8.4 + 3/4[2p\text{H} + p\text{SO}_4]$$ \[8\]

For alunite, $p(\text{K}^+)(\text{Al}^{3+})^3(\text{OH})^6(\text{SO}_4^{2-})^2 - 2pK_w$

$$= 3[p\text{Al} + p\text{OH} + p\text{SO}_4] + [p\text{K} + p\text{OH}] - [2p\text{H} + p\text{SO}_4]$$

$$= 57.4$$

which, on rearrangement, yields

$$[p\text{Al} + p\text{OH} + p\text{SO}_4] = (19.13 - 1/3 [p\text{K} + p\text{OH}]) + 1/3[2p\text{H} + p\text{SO}_4]$$ \[9\]

For gibbsite,

$$[p\text{Al} + p\text{OH} + p\text{SO}_4] = 4.77 + [2p\text{H} + p\text{SO}_4]$$ \[10\]

Soil solution ion activities are plotted with $[p\text{Al} + p\text{OH} + p\text{SO}_4]$ as a function of $[2p\text{H} + p\text{SO}_4]$, along with stability lines
Figure 9.5. Soil solution activities relative to stability line for Al-hydroxy sulfate minerals and gibbsite in two acid sulfate soils. Plotted data points above a line indicated supersaturation, and points below a line indicated undersaturation. Assumed $pK^+ + pOH = 12.3 \pm 1.0$.

for Al-hydroxy sulfate minerals and gibbsite in a manner similar to those reported by Hue et al. (1985), and Wolt et al. (1992). The stability line for alunite is fixed by using the average value of $[pK^+ + pOH = 12.3 \pm 1.0]$ for soil solution from Table 9.5.
As seen in Fig. 9.5, all the experimental points were positioned between the theoretical line for jurbanite and alunite equilibria. The points for the unamended Bg soil appeared slightly above the jurbanite isoline (where $2pH + pSO_4 < 11.5$), whereas those at the higher pH due to lime and sesbania treatments occurred on or near the alunite isoline. Thus, as discussed earlier, increasing soil pH by lime or sesbania application (Table 9.5) may transform jurbanite to alunite. These observations suggest that soil solution $Al^{3+}$, $SO_4^{2-}$ and $H^+$ activities as affected by lime and sesbania treatments (when $2pH + pSO_4 > 11.5$) closely parallel that of alunite. If we assume that such a line represents an equilibrium between an unknown solid phase (alunite-like) and the solution, then the unknown solid phase has a log $K_{sp} = -81.4 \pm 1.6$, which is very close to $-80.9$ given by Lindsay (1979), but much larger than $-85.6$ as suggested by Nordstrom (1982) or $-85.4$ reported by Adams and Rawajifih (1977) for crystalline alunite. Nevertheless, the close association between the experimental points under the present study and the alunite phase line of Figure 9.5 suggests the existence of an Al-controlling phase similar to alunite, but more soluble than the crystalline form of alunite as described by Adams and Rawajifih (1977) and Nordstrom (1982). In addition, the X-ray diffraction pattern of the clays at 90 days after incubation revealed no sulfate-bearing phase, which is expected if the phase is noncrystalline.
9.5 Summary and conclusions

Both potential and actual acid sulfate soils of the Bangkok Plain were acidified strongly by pyrite oxidation after only 90 days of incubation. The soils were characterized by high concentrations of Al, Fe, Mn and low concentrations of Ca. For successful crop production either lime or green manure applications will be necessary. The use of locally available, green manure species as a "self-liming material" is a promising strategy for alleviation of Al toxicity and raising basic cations in the soil solution.

XRD analysis showed that both soils were similar in their mineralogical composition. The clay fraction contained mainly mica, smectite, and kaolinite, with minor amounts of illite and gibbsite. Liming or green manuring apparently did not change mineral compositions in spite of a strong and rapid acidification in the unamended soil. Yellowish jarosite mottles were a common feature as incubation progressed. Jarosite may form by chemical precipitation from the soil solution if SO$_4$$^{2-}$ concentration is very high and pH below 5. Based on the pIAP and stability diagrams, the results suggest the existence of an alunite-like mineral which has similar chemical composition, but a higher solubility ($pK_{sp} = 81.4$) than crystalline alunite ($pK_{sp} = 85.4$). The proposed alunite is believed to govern Al$^{3+}$ activities in acid sulfate soils that were influenced by lime or green manure application.
References


Osborne, J.F. 1985. End of assignment report to the acid sulfate soils improvement project. Dept. of Land


APPENDIX A

1. Soil Information and Profile Descriptions of Bang Pakong Series.

Soil information

Soil Name: Bang Pakong Series; Field symbol: Bg

Taxonomy: Typic Sulfaquents

Location: Bang Pakong Soil Conservation Center, Chachoengsao Province

Physiography: Formerly mangrove forest

Topography: Flat

Slope: 0 - 1%

Elevation: Approximately 1 - 2 m above mean sea-level

Air-temperature: 27 °C

Water table: Close to the surface

Drainage: Poorly drained; Permeability: Slow

Land use: Transplanted and broadcast rice

Parent materials: Brackish water deposits

Described by: Soil Survey Staff, Dept. of Land Development

Profile descriptions

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<td>50% dark grayish brown (10YR 4/2) and 50% brown to dark brown (10YR 4/3) silty clay; many, coarse, faint, diffuse, dark reddish brown (5YR 4/3) mottles; weak coarse, angular blocky; sticky, non-plastic; few medium vertical, inped and exped, continuous, tubular pores; many very fine roots, pores frequently filled with fecal pellets; clear, smooth boundary.</td>
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B1  10 - 18  70% dark grayish brown (10YR 4/2) and 30% brown to dark brown (10YR 4/3) silty clay; many coarse, distinct, clear to diffuse, reddish brown (5YR 4/4 - 5YR 4/3) mottles and glossy coatings on pore walls; locally many coarse, distinct, clear, strong brown (7.5 YR 5/6) mottles; weak, coarse angular blocky; sticky, non-plastic; common, fine to medium, vertical, inped and exped, continuous, tubular pores; many very fine roots; many pores filled with fecal pellets; clear, smooth boundary.

B2g  18 - 30  grayish brown (10YR 4/2) and locally very dark gray (10YR 3/1) silty clay; many, coarse, distinct, clear to diffuse, reddish brown (10YR 4/4 - 10YR 4/3) glossy coatings on pore walls; only at a few spots in the wall of the pit; many, coarse, prominent, sharp to clear, yellow (2.5Y 8/6) jarosite on ped faces and in layers (appr. 3 mm thick) sandwiched in between the matrix and the reddish brown coatings on pore walls; jarosite is sometimes associated with half decayed wood (root) fragments; weak, coarse, angular blocky; slightly sticky, non-plastic; common, fine to coarse, continuous, vertical inped, tubular, mostly open pores; pores often filled with fecal pellets and root remnants; few roots, locally pieces of soft half decayed wood (up to 10 cm in diameter); moderate to very rapid permeability; gradual, irregular boundary.

C1g  30 - 60  greenish gray (5GY 4/1) clay; unmottled; weak, coarse prismatic; slightly sticky, non-plastic; common, fine to coarse, continuous vertical, inped, tubular pores, sometimes filled with fecal pellets or half decayed roots; locally remnants of Xylocarpus and Nipa roots; moderate to rapid permeability.

C2g  60-  greenish gray (5GY 4/1) clay; unmottled; locally many soft shell fragment and black pockets of organic matters; rapid to very rapid permeability; at many spots in the wall of the pit FeS suspension seeps from these pockets of organic matter into the pit.
2. Soil information and Profile Descriptions of Rangsit Very Acid-Phase Series.

Soil information

Soil Name: Rangsit; Field symbol: Ra
Taxonomy: Sulfic Tropaquepts
Location: Ongkharak Acid Sulfate Soil Experiment Station, Nakhon Nayok Province
Physiography: Former tidal flat
Topography: Flat
Slope 1%; Elevation: 2 m above mean sea-level
Air-temperature: 28 °C
Water table: 80 cm
Drainage: Poorly drained; Permeability: slow
Land use: Paddy field, broadcast rice
Parent materials: Fresh and brackish water deposits
Described by: Soil Survey Staff; Dept. of Land Development

Profile descriptions

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<td>black (10YR 2/1) clay; common, fine, distinct, sharp, dark yellowish brown (10YR 3/4) rootrust; common, medium, faint, diffuse, dark yellowish brown (10YR 3/4) mottles on ped faces; common, medium, distinct, diffuse, yellowish brown (10YR 5/6) mottles on ped faces (mainly in the lower part of the horizon); weak, coarse, and moderate, fine to medium, angular to sub-angular blocky; slightly sticky, plastic to slightly plastic; few, fine, mainly vertical, mainly inped tubular pores; abundant fine roots, mainly along ped faces; very slow permeability; clear, wavy boundary.</td>
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B1g  30 - 60  grayish brown (10YR 5/2) clay; many, coarse, prominent, clear, dark yellowish brown (10YR 4/6) mottles; few, medium, distinct, clear yellowish brown (10YR 5/6) mottles; weak, coarse, and moderate, fine, angular blocky; slightly sticky, slightly plastic; common, continuous slickensides; few to common, fine, vertical, inped and exped tubular pores; few fine to medium pores filled with black (10YR 2/1) clay, very few roots, mainly in the upper part of the horizon; slow permeability; clear, wavy boundary.

B2g  60 - 85  grayish brown (10YR 5/2) clay; mainly in the upper part of the horizon common, coarse, prominent, clear, red (10R 4/6) mottles; common, medium to coarse, distinct, diffuse, yellowish red (5YR 4/6) mottles, surrounded by medium to coarse, distinct, diffuse, yellowish brown (10YR 5/6) mottles, both in the matrix, along pores and along ped faces; common, medium to coarse, prominent, sharp and clear, yellow (5Y 8/6) jarosite, mainly as pore-fillings and surrounded by yellowish brown (10YR 5/6) mottles; moderate, coarse and medium, angular blocky; slightly sticky, plastic; common, broken slickensides; few to common, fine to medium, continuous, vertical, mainly exped, tubular pores; moderately slow to moderate permeability; no roots; gradual, smooth boundary.

B3g  85 - 115  grayish brown (10YR 5/2) clay; few to common, medium to coarse, distinct, diffuse, yellowish red (5YR 4/6) mottles and common, medium to coarse, distinct, diffuse, yellowish brown (10YR 5/6) mottles along vertical pores; common, medium to coarse, distinct, sharp, yellow (5Y 8/6) jarosite; weak, coarse prismatic; sticky, non-plastic; patchy slickensides; common, fine to coarse, continuous, vertical, inped and exped, tubular pores; very few roots; moderate to moderately rapid permeability; gradual, smooth boundary.

B4g  115 - 170  grayish brown (10YR 5/2) clay; few, medium to coarse, distinct, diffuse, yellowish brown (10YR 5/6) mottles; mainly along vertical pores; few, medium to coarse, distinct, sharp, yellow (5Y 8/6) jarosite mottles;
locally broken coatings of jarosite and yellowish brown (10YR 5/6) rust on prism faces; common, distinct, hard, yellowish brown (10YR 5/6) coatings (1 - 2 mm thick) along fine to medium, vertical pores, with a very thin dark yellowish brown (10YR 3/4) coating inside; weak, coarse prismatic; sticky, non-plastic; common, fine to coarse, continuous, vertical, inped and exped pores; very few roots; moderately rapid permeability; diffuse, smooth boundary.

Cg 170+ gray (5Y 5/1) clay, unmottled.
APPENDIX B

Aluminum phytotoxicity in acid tropical soils: A review

ABSTRACT

Aluminum (Al) toxicity is a major factor limiting plant growth in acid soils. Thus, knowledge of Al reactions in soils and plants are essential for increasing soil productivity and crop production. This review discusses (i) soil parameters (e.g., pH, soluble Al concentration and activity, exchangeable Al, and Al saturation percentage) that have been used to indicate Al phytotoxicity, (ii) estimation of lime quantities required to correct soil acidity and Al toxicity, (iii) Al species in the soil solution and their differential toxicities, and (iv) Al tolerance mechanisms of various plants. Future work on Al research is suggested.

Key words: Al activities; Al phytotoxicity indices; Al tolerance mechanisms; monomeric hydrolytic species;

Introduction

Aluminum toxicity is probably the most important growth-limiting factor to plants in acid soils of the tropics (Foy, 1988). The problem is particularly severe below pH 5.0, but has been reported to occur at pH as high as 5.5 in some soils (Foy, 1984). The critical soil pH at which soluble or exchangeable Al becomes toxic depends upon various factors, including clay minerals, organic matter levels, concentrations
of other cations, anions and total salts, and particularly the plant species or cultivars (Kamprath and Foy, 1985). Generally, Al toxicity adversely affects roots more than shoots. The Al-affected roots often appear coralloid, with many stubby lateral roots and no fine branching (Foy, 1984). Aluminum-damaged roots can explore only a limited volume of soil and are inefficient in absorbing nutrients and water. Furthermore, excess soil Al interferes with uptake, transport and utilization of essential nutrients (Ca, Mg, K, P and Fe) and may inhibit microbial processes that supply nutrients to plants (Foy, 1988).

**Tests for Aluminum Toxicity by Acid Soils**

Conventional tests for Al toxicity in soils include pH, exchangeable Al, Al saturation percentage of CEC, dilute acid extractable Al (Wright, 1989), and soil-solution Al (Bruce et al., 1988). For soils having similar parent materials and clay mineralogy, pH alone or absolute levels of Al extracted by KCl or other unbuffered salts may be adequately indicative of Al toxicity to a given plant (McCormick and Amendale, 1983). In general, a more useful predictor of Al toxicity is the percentage of the cation exchange capacity (CEC) occupied by Al (Evans and Kamprath, 1970; Kamprath and Foy, 1985). Aluminum saturation is determined by displacing soil Al with a neutral, unbuffered salt (such as 1M KCl), and expressing the Al as a percentage of the CEC (measured by 1M NH₄OAc, pH
7.0) or as a percentage of the effective CEC (Sum of Ca, Mg, K, and Na extracted with NH₄OAc and KCl-extractable Al). To be effective, the Al saturation percentage must be applied within rather narrowly defined set of conditions because the critical Al saturation associated with toxicity varies with soil type, plant species and even with genotype (Foy, 1987). Critical soil exchangeable Al levels for alfalfa reportedly ranged from 0.2 - 0.9 cmolₖg⁻¹ or 4 to 19% Al saturation (Foy, 1964). Unfortunately, neither exchangeable Al nor Al saturation remains constant when applied to a range of different soils in defining critical soil Al levels.

Evans and Kamprath (1970) found that when the Al saturation reached 60% of the effective CEC, the Al concentration in the soil solution was generally greater than 1 µg g⁻¹ which is toxic to most plants. The relationship was fairly constant for kaolinitic, and mixed montmorillonitic mineralogies. This finding led Fox (1979) to suggest that Al saturation greater than 60% would be considered as detrimental effect to most crops and 10 - 20% to highly sensitive crops (Figure 1).

Exchangeable Al has been used to calculate lime requirements for soils with low permanent charge and relatively high pH-dependent charge (Reeve and Sumner, 1970). In this method, lime quantities are added as multiples of the amount of exchangeable Al on a chemically equivalent basis. After the lime has had sufficient time to react, the amount of
Figure 1. Relationship between Al saturation of two Ultisols in Pennsylvania and relative corn grain yield (Fox, 1979).

Various studies have shown that lime rates chemically equivalent to 1.5 to 3 times the exchangeable Al must be added to completely neutralize Al (Table 1). The greater lime rates can be explained by the buffering properties of acid soils.
Exchangeable Al is responsible for the buffering in the pH range of 4.0 to 5.6, while hydroxy-aluminum and aluminum-organ complexes control the buffering pH in the range of 5.6 to 7.6 (Jackson, 1963). Studies on Ultisols showed that when soil pH < 5.3, lime reacted with both exchangeable Al and pH-dependent sources of acidity (Kamprath, 1970). On average, lime must be added at a rate chemically equivalent to twice the exchangeable Al content to eliminate Al toxicity.

**Table 1.** Liming factor (Al in cmol, kg⁻¹ x factor) required to give equivalent of calcium carbonate to reduce aluminum saturation to less than 10 %

<table>
<thead>
<tr>
<th>Location</th>
<th>Soil</th>
<th>pH</th>
<th>Al (cmol, kg⁻¹)</th>
<th>Al saturation (%)</th>
<th>Factor</th>
<th>Final pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brazil</td>
<td>Red-Yellow Latosol</td>
<td>4.0</td>
<td>0.7</td>
<td>70</td>
<td>3</td>
<td>4.9</td>
</tr>
<tr>
<td></td>
<td>Red-Yellow Latosol</td>
<td>4.4</td>
<td>0.9</td>
<td>75</td>
<td>2</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>Dark-Red Latosol</td>
<td>4.0</td>
<td>1.9</td>
<td>86</td>
<td>2</td>
<td>5.0</td>
</tr>
<tr>
<td>Columbia</td>
<td>Oxisol</td>
<td>4.3</td>
<td>3.5</td>
<td>78</td>
<td>2</td>
<td>5.3</td>
</tr>
<tr>
<td>Panama</td>
<td>Latosol</td>
<td>5.1</td>
<td>1.2</td>
<td>53</td>
<td>1.5</td>
<td>5.9</td>
</tr>
<tr>
<td></td>
<td>Latosol</td>
<td>5.0</td>
<td>3.0</td>
<td>64</td>
<td>1.5</td>
<td>6.0</td>
</tr>
<tr>
<td>United States</td>
<td>Ultisol</td>
<td>4.5</td>
<td>0.9</td>
<td>82</td>
<td>2.0</td>
<td>5.9</td>
</tr>
<tr>
<td></td>
<td>Ultisol</td>
<td>4.7</td>
<td>1.0</td>
<td>78</td>
<td>2.0</td>
<td>6.0</td>
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<tr>
<td></td>
<td>Ultisol</td>
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<td>73</td>
<td>1.5</td>
<td>5.7</td>
</tr>
<tr>
<td></td>
<td>Ultisol</td>
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<td>4.2</td>
<td>54</td>
<td>1.5</td>
<td>5.6</td>
</tr>
<tr>
<td>India</td>
<td>&lt; 5.0</td>
<td></td>
<td></td>
<td></td>
<td>2.0</td>
<td>5.3</td>
</tr>
<tr>
<td>Natal</td>
<td>Oxisol</td>
<td>&lt; 5.0</td>
<td></td>
<td></td>
<td>3.3</td>
<td>-</td>
</tr>
</tbody>
</table>

**Aluminum Speciation and Al Tolerance of Plants**

It is generally agreed that some measure of Al activity in
soil solution is more indicative of potential toxicity than concentrations of water soluble Al or exchangeable Al or Al saturation percentage (Adams, 1981). Adams and Lund (1966) found that the critical Al activity which limited cotton root growth in soil solution was the same as in nutrient solution (> 0.15 x 10^{-5} M) (Fig. 2). Toxicity of water soluble Al is further reduced by chelation with organic acids or other ligands (Hue et al., 1986); and this process must be taken into account when calculating the activity of the Al^{3+} ion. Many investigators (Parker et al., 1988; Kinraide and Parker, 1989) have reported that the calculated activity of the Al^{3+} ion is the best indicator of Al toxicity. However, recent evidence also indicates toxicity from monomeric hydrolytic species as Al(OH)^{2+}, Al(OH)^{+}, and from polymeric hydrolytic species of Al (Parker et al., 1989). At low OH:Al, and P:Al molar ratios, most Al is present as monomeric species; at high OH:Al and P:Al ratios, soluble Al polymers may develop. These polymers tend to precipitate with time but often remain soluble in dilute solutions (White et al., 1976). The AlSO_4^{2-} species is generally considered as non-toxic or much less toxic than Al^{3+} (Cameron et al., 1986).

The total concentration of monomeric Al in acid soil solutions is the sum of various monomeric species: Al^{3+}, Al(OH)^{2+}, Al(OH)^{+}, and Al(OH)_3^{0}. Complex ions of Al with SO_4^{2-} and F^- also exist when these anions are presented (Tanaka et al., 1987). Thus, the total soluble Al concentration over the
Figure 2. Effect of molar activity of Al in subsoil solutions in situ and in subsurface nutrient solutions on cotton primary root growth (Adams and Lund, 1966).

pH range of 4-6 is described by:

\[
[\text{Total soluble } Al] = [Al^{3+}] + [Al(OH)^{4+}] + [Al(OH)_2^{2+}] + [Al(OH)_3^{+}] + [Al(OH)_4^{-}] + [AlSO_4^{2-}] + [AlF_6^{3-}]
\]  \[1\]

If the total concentration of monomeric Al in soil solution, pH, ionic strength, $SO_4^{2-}$ and $F^-$ concentration, are known, the concentrations, activity coefficients, and activities of
individual species in Eq. (1) can be calculated. Blamey et al. (1983) reported a good correlation of soybean root elongation with the sum of activities of all monomeric hydrolytic species ($\Sigma a_{Al\ mono}$). Alva et al. (1986a) reported a better prediction of Al phytotoxicity by using $\Sigma a_{Al\ mono}$ over the use of the measured total soluble Al concentration, or the measured individual Al species in solution.

Solution cultures may provide well controlled environments for studying effects of Al on plant growth (Bell and Edwards, 1987). Such experiments often use Al concentrations greatly in excess of those commonly found in acid soil solutions, coupled with high phosphate concentrations (Blamey et al., 1983). Those studies also correlated plant growth with the nominal (added) Al concentration, or the total measured Al concentration (Alva et al., 1986a).

On the other hand, when plants are grown in nutrient solutions in which the activity of monomeric Al species can be measured and controlled, comparisons between plant species or growth phases are possible. For example, Alva et al. (1987) showed that the critical $\Sigma a_{Al\ mono}$ for growth of roots and shoots of soybean cultivar "Fitzroy" were 5 and 9 μM, respectively, whereas the critical $\Sigma a_{Al\ mono}$ for nodulation was 0.4 μM. Other studies have also shown that nodulation is more sensitive to Al than the host plant growth (Suthipradit, 1989). By contrast, Franco and Munns (1982) showed that the primary Al limitation was on host plant and not on nodulation.
Reports on toxic Al concentrations associated with yield reduction are extensive for a wide range of plant species. Asher (1981) reported that toxic Al concentrations for various species grown in flowing solution culture were: maize, > 20 \( \mu M \); cassava, > 20 - 30 \( \mu M \); soybean > 40 \( \mu M \); sweet potato, > 40 - 80 \( \mu M \); ginger and taro > 80 \( \mu M \). While comparisons can be made among species of plants grown in a common solution or similar solutions, comparisons between different studies are difficult. Differences in solution pH, ionic strength, phosphate concentration, and calcium concentration make such comparisons nearly impossible. For example, Alva et al. (1986b) showed that the value of \( E_{A_{\text{mono}}} \) necessary to reduce root elongation by 50% varied with increasing Ca concentrations (0.5 to 15 mM Ca); this Al varied from 12 to 17 \( \mu M \) for soybean, < 8 to 16 \( \mu M \) for sunflower, < 7 to 15 \( \mu M \) for subterranean clover, and 5 to 10 \( \mu M \) for alfalfa.

Plant species and cultivars within species vary greatly in their ability to cope with Al-toxic soils as shown in Figure 3 for six rice cultivars (Fageria et al., 1987). The physiological processes by which certain plants tolerate high levels of Al are still unclear. Fageria et al. (1988) have summarized various proposed mechanisms responsible for aluminum tolerance in plants. These mechanisms include pH increases, Al trapping in nonmetabolic sites within plant cells, greater P, Ca, and Mg uptake and transport and use
efficiency, lower root CEC, greater root phosphate activity, higher internal concentrations of Si, and higher organic acid contents. Aluminum tolerance in higher plants appears to be due to a combination of both exclusion and internal tolerance mechanisms (Taylor, 1988). The exclusion mechanism refers to the immobilization of Al at the root-soil interface. Binding of Al by cell walls, selective permeability of plasma membranes, plant induced pH barriers, and exudation of
chelating ligands are known to play a role in Al exclusion mechanisms. Chelation of Al by carboxylic acids or Al-binding proteins of the cytosol, compartmentation of Al in the vacuole, and evolution of an Al-tolerant enzyme systems are possible internal Al tolerance mechanisms.

Future Knowledge Needs

Activities of Al species in solution probably give the best indicator of soil acidity. Soil solution extraction is however, too time-consuming to be used as a routine test. A relatively quick but reliable chemical test to identify potentially Al-toxic soils is desirable. The indirect methods currently used to calculate phytotoxic Al in soil solution need to be strengthened by direct measurements. A better understanding of the role of soluble and solid phase organic components in controlling Al phytotoxicity is also needed. Answers should be sought regarding the relative toxicity of $\text{Al}^{3+}$, $\text{Al(OH)}^{2+}$ and $\text{Al(OH)}_{2}^{+}$ to different plant species as well as the toxicity of Al polymers. Research efforts should be focussed on the rhizosphere rather than on the bulk soils.

Aluminum tolerant plants are a partial answer to soil Al toxicity. Some combinations of agronomic practices to minimize soil acidification, such as additions of lime or other soil amendments to reduce Al toxicity, are needed to overcome soil Al toxicity and to increase crop production in the long term.
References


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