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INFLUENCE OF VARIOUS WATER MANAGEMENT AND AGRONOMIC PACKAGES ON THE
CHEMICAL CHANGES AND ON THE GROWTH OF RICE IN ACID SULPHATE SOILS

Proefschrift

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Statements

1. Up to now, undisturbed lysimeters (soil columns) for the study of water and solute movement in the soil have been underused in research on soils and especially in acid sulphate soils.
2. Mulching the surface soil of acid sulphate soils during the dry season is a good measure to avoid the accumulation of toxic elements in the surface soil.
3. Research on problem soils without site characterization has limited application.
4. Reclamation of problem soils without proper identification of the soil properties is apt to be disappointing.
5. Agricultural research in developing countries should aim at raising the poor farmers' standard of living.
6. Small scale development does not produce large errors.
7. Poor farmers often do not benefit from high technology.
8. Correction of errors and mistakes will be impeded if the real causes of mistakes are not exposed.
9. Higher scientific degrees help the holder to acquire recognition and social status. It is not, however, a good yardstick to measure ability in practice.
10. In the Far-East, people distinguish a degree holder from a learned man, and the latter from a talented man. It is a good way of judging scientists.
11. F. Engels wrote: "Nature will avenge itself on our thoughtless acts if we do not act in conformity with its laws". In line with that statement one can say that it is necessary to take measures in preserving ecology as soon as possible, otherwise our ecosystem will further be destabilized.

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Acid sulphate soils are derived from marine and estuarine sediments containing high concentrations of reduced sulphur components. Upon drainage and aeration they show a definite and severe acidification due to the oxidation of sulphides (mainly pyrites, FeS_2) leading to the formation of sulphuric acid. These soils have pH values below 3.5 (if Entisols) or 4 (if Inceptisols) in the upper 50 cm. They are found both in the temperate and tropical regions, but the vast majority of such soils are in the economically underdeveloped tropics where mounting population pressure will require maximum utilization of all available land in the near future.

About 13 million hectares of potential agricultural lands in tidal swamp areas are not developed because of acid sulphate soils (Table 1.1). There are about 5 million hectares of these soils in south and southeast Asia, about 3.7 million hectares in Africa and about 2 million hectares in south America (van Breemen, 1980).

Although physiographic and hydrologic conditions are generally favourable for rice growing in acid sulphate soils, a number of unfavourable factors such as soil acidity, salinity, aluminium toxicity, iron toxicity, hydrogen sulphide concentration and nutrient deficiencies associated with high acidity, preclude efficient utilization of such land.

The high degree of acidity (or potential acidity) of acid sulphate soils makes reclamation through liming economically impractical in most cases. The only practical way to manage these soils is by proper drainage and water management. Maintaining a high water table can control

Table 1.1 World distribution of acid sulphate soils¹⁾ (millions ha).

Region	Length of growing periods (days)				total
	< 90	90-180	180-300	> 300	
Asia and Far East	0.0	0.2	5.1	1.4	6.7
Africa	0.4	0.7	1.5	1.1	3.7
Latin America	0.0	0.1	0.8	1.2	2.1
North America	0.0	0.0	0.0	0.0	0.1
Other regions	-	-	-	-	0.0
World total	0.4	1.1	7.4	3.7	12.6

1) Adapted from Beek et al. (1980), based on data from FAO/UNESCO soil map of the world. Growing period data according to FAO Agro- ecological zone project, Rome

the oxidation of pyrite (the sulfur source in these soils). Where feasible, drainage and removal of acidity by leaching can be used. Proper water management and drainage control have made rice production possible in large acid sulphate areas of Thailand and Vietnam.

This thesis is the outcome of various studies. In Chapter 2 an investigation about the influence of different water management and agronomic packages on the chemical changes and on the growth of rice in acid sulphate soil is given. A simple, low-cost lysimeter was developed to investigate the above objectives. Various methods of water managements and agronomic practices will be pointed out.

Chapter 3 describes soil column experiments carried out to study the evaporation and acidification process in acid sulphate soil.

Chapter 4 deals with the effects of acid sulphate flood water on the chemical changes and on the growth of rice in acid sulphate soils.

Chapter 5 presents results of pot experiments on the effect of different methods of application of rock phosphate fertilizers on the transformation of phosphorus in acid sulphate soils.

Chapter 6 gives a simulation of the oxidation and acidification processes in acid sulphate soils.

Chapter 7 contains the conclusions and recommendations for future research.

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2 INFLUENCE OF VARIOUS WATER MANAGEMENT AND AGRONOMIC PACK-
AGES ON THE CHEMICAL CHANGES AND ON THE GROWTH OF RICE IN
ACID SULPHATE SOILS

Abstract

Forty undisturbed soil cores of two acid sulphate soils (60 cm diameter, 90 cm deep) in the Philippines were used to study the influence of drainage, liming, percolation and mulching on the growth of IR 36 rice cultivar and on the chemical changes during two leaching periods and three cropping seasons. Grain yields differed greatly among the two soils and three cropping seasons. In Aparri soil, there were no marked effect of drainage, liming and agronomic practices on grain yield over three cropping seasons. This was associated with high pH in the surface soil and minimal pyrite oxidation in the subsoil. In Sinacaban soil, during the first season, grain yields were hardly affected by treatments because the soils did not undergo drying and oxidation. During the second and third season, the influence of different treatments on grain yields was very pronounced. Deep drainage treatment gave the poorest yields in both second and third crops. Highest yields were obtained in the surface flushing treatment, the next highest yields with shallow drainage. Contrary to expectation, the grain yield in deep drainage treatments was lower with, than without percolation at application of 2.5 tons of lime/ha. Mulching increased grain yield by 67 and 30 percent for the second and third crops, respectively. In the deep drainage treatment, only a high amount of lime, 2.5 tons/ha, produced a yield exceeding the equivalent of about 1 t/ha. The frequency of occurrence of successful crops under different practices revealed the superiority of the flushing treatment. The concept of average min-

eral stress index (AMSI) was introduced as a measure for toxic elements in acid sulphate soils (pH, Fe^{2+} and Al^{3+}). This index gave certain indications of grain yield: below AMSI = 40 reasonable yields were obtained, above AMSI = 100 the crop failed completely.

The chemical changes of different treatments were monitored during the two leaching periods and during the growing seasons for different depths along the soil profile and for the surface water. The chemical changes varied with soil and management practices. Deep drainage in Sinacaban soil produced a large amount of acidity, and the frequency of occurrence of pH less than 3.5 was 100 percent for layers below 40 cm depth. Shallow drainage treatment did not cause severe oxidation in the subsoil layers and produced less acidity. The reduction process followed the same trend with other experiments for surface soil. Even with prolonged submergence, reduction took place very slowly in the subsoil layers. Acidity remained very high for a long period (9 months). In addition to the high acidity, iron (II) was also very high, which hampered the growth of rice. Concentration of aluminium decreased as the pH of the soil increased. Minimizing pyrite oxidation is therefore recommended to avoid the adverse effects of toxic elements.

2.1 Background of research on acid sulphate soils

2.1.1 Acid sulphate soils and their distribution

Acid sulphate soils are usually derived from marine and estuarine sediments containing high concentrations of reduced sulphur compounds. They show a definite and severe acidification upon drainage and aeration, owing to the oxidation of sulphides (mainly pyrites, FeS_2), with formation of sulphuric acid. They are found both in the temperate and tropical regions, but the vast majority in the tropics (Kawalec, 1973). They cover more than 15 million hectares of flat land well suited to year-long rice growing. Because of the high acidity and large amounts of toxic substances in the soil, they are left uncultivated or put only to marginal use. Farmers have devised means of farming part of these soils for lowland rice but generally obtain very low returns.

2.1.2 Causes of low productivity

The low productivity of acid sulphate soils may be due to one or more of the following unfavourable factors: soil acidity, salinity, aluminium toxicity, iron toxicity and low nutrient status.

Soil acidity

Soil acidity per se is harmful to plants and impairs the absorption of nutrients, especially of calcium and phosphorus (Arnon and Johnson, 1942, Arnon et al., 1942). Rorison (1973) pointed out that plants may tolerate relatively large concentrations of H^+ ions, as long as the concentrations of other cations are large, and the concentration of toxic polyvalent cations is small. Rice in its vegetative growth stage was found not to be affected by H^+ concentrations up to pH 3.5, although the high acidity suppressed the uptake of metallic cations (Thawornwong and van Diest, 1974). A low pH aggravates the harmful effects of organic acids (Tanaka and Navasero, 1967). Low pH inhibits the conversion of ammonium to nitrate, so that NH_4^+ ions accumulate. Some plants take up both ammonium and nitrate ions, but calcicole species may give poor or no growth when supplied with NH_4 -N at pH 4.2 whereas calcifuge plants flourish with NH_4 -N at that pH (Rorison, 1973).

Salinity

There are large increases in soluble salts when pyritic soils are drained and oxidized. Ponnampetuma et al. (1973) report specific conductance levels exceeding 10 mS/cm in some acid sulphate soils.

Rice is a moderately salt tolerant crop (Richards, 1954). It is very tolerant during germination but sensitive at the 1-2 leaf stage. The tolerance of rice progressively increases during the tillering and elongation stages of development and again decreases at the time of floret fertilization. Excess salt retards growth and depresses yield (Iwaki et al., 1953; Iwaki, 1956; Pearson, 1961). Zashariah and Sankarabramoney (1961) found that the salt tolerance of all varieties of paddy increases with maturity. Sprouted rice seed grew normally in a culture solution when the specific conductivity was less than 4 mS/cm. Between 4 and 11 mS/cm, growth was retarded, and at a conductivity

greater than 11 mS/cm the seedling failed to grow (Pearson, 1959). These results were confirmed by IRRI (1967).

Aluminium toxicity

Aluminium is normally the major exchangeable cation in very acid soils. It becomes more soluble at low pH. The relationship between pH and Al concentration in a soil solution is given as:

$$pAl = 2pH - 4.41 \text{ (Mai thi My Nhung and Ponnampuruma, 1966).}$$

In various crops (Nagata, 1953; Nomoto and Kisida, 1959) including rice (Cate and Sukhai, 1964), aluminium toxicity is first evidenced by root injury (coralloid stunted roots) and then by characteristic symptoms on the leaves.

Aluminium toxicity is reportedly due to the inactivation of phosphorus, especially in the roots (Wright, 1943) and also to the coagulation of proteins (Aimi and Murakami, 1964).

The critical concentrations of Al in solution and the critical contents of Al in plants vary for different species. Aluminium toxicity to rice was first reported by Miyake in 1916, who showed that 1.2 mg Al/l in solution was toxic. Cate and Sukhai (1964) stated that in the temporary absence of nutrient cations, 1 to 2 mg/l of soluble Al markedly inhibits the growth of rice roots. Tanaka and Navasero (1966) considered 30 mg Al/l in rice shoots as a critical value. Above this level, Al-toxicity symptoms often developed. The deleterious effect of Al on the growth of rice was especially noticeable in the seedling stage (Thawornwong and van Diest, 1974). A concentration of 2 mg Al/l, either in chloride or in chelate form did not affect the growth of rice when applied after the seedling stage (Thawornwong and van Diest, 1974).

The critical value was found to vary with the P status of the plant, and with the Fe concentration and pH in the culture solution. Liming a low-pH soil reduces or eliminates the detrimental effects of aluminium (Wright, 1937). Application of phosphorus lowers the solubility of aluminium in the growth medium and results in relief from toxicity (Wright, 1937). A phosphate-aluminium interaction was reported earlier by Blair and Prince (1927) who found that Al toxicity can be overcome

by heavy applications of soluble phosphates or by the application of basic materials such as lime and basic slag. This is attributed in part to the precipitation of aluminium phosphate in and on the roots (Nomoto and Kisida, 1959; Vlamis, 1953; Wright, 1943). The application of acid-forming materials increased the concentration of active aluminium in the soil (Blair and Prince, 1927). Struthers and Sieling (1950) found that the concentrations of Al, Mn, and Ca in the soil solution were markedly increased when gypsum was added to the soil: a cation exchange effect by the increased Ca and total salt concentration.

Iron toxicity

The concentration of ferrous iron in flooded soils is highly sensitive to pH changes. The relationship between pH and concentration of dissolved Fe^{2+} is as follows (Mai thi My Nhung and Ponnampuruma, 1966):

$$\begin{aligned} \text{pFe}^{2+} &= 2 \text{ pH} - 10.8 \quad (\text{Fe}_3(\text{OH})_8 \text{ present}) \\ \text{or} \quad \text{pFe}^{2+} &= 2 \text{ pH} - \text{pH}_2\text{S} - 3.52 \quad (\text{FeS present}) \end{aligned}$$

Mai thi My Nhung and Ponnampuruma (1966) reported that the Fe^{2+} concentration reached 800 mg/l after 5 weeks of submergence. Fe^{2+} values of 800 to 1700 mg/l leachate were found in flooded conditions, with or without incubation (Tanaka and Navasero, 1966). Fe^{2+} concentrations of 5000 mg/l, 2 weeks after submergence, were reported by Ponnampuruma et al. (1973), but values of 500-1000 mg/l are more common, and some soils apparently give very little. The peak values were observed after 30 days of submergence in acid sulphate soils in Kerala (Kaberathuman and Patnaik, 1978). Iron toxicity in submerged acid sulphate soils is the limiting factor for rice (IRRI, 1964, 1965). Concentrations of ferrous iron above 500 mg/l are indicated as toxic (Tanaka and Navasero, 1966b; Mai thi My Nhung & Ponnampuruma, 1966). Tanaka et al. (1966) observed that rice leaves containing more than 300 mg/l Fe^{2+} often exhibit iron toxicity symptoms. The physiological disorder of rice known as bronzing in Ceylon and penyakit merah in Malaysia is caused by excess iron (Lockard, 1956; Ponnampuruma et al., 1955).

There are many factors that aggravate or alleviate iron toxicity. A low

potassium content and the presence of sulfide induced iron toxicity (Inada, 1965; Mulleriyawa, 1966; Tanaka and Navasero, 1966; Tanaka et al., 1968). Iron toxicity can be alleviated by liming and by the addition of manganese dioxide (Ponnamperuma et al., 1965). Lime increases the pH and lowers the concentrations of dissolved Fe^{2+} ; it also counteracts physiologically the adverse effects of excess iron (Tanaka and Navasero, 1966). In a pot experiment, Sahrawat (1979) studied the effects of two water regimes (continuous flooding and flooding with intermittent soil drying) on iron toxicity to rice in an acid sulphate soil. He found that rice could be planted after keeping an acid sulphate soil flooded for a few weeks, when dissolved iron had dropped below a toxic level; drying and reflooding on the other hand aggravated soil acidity and kept iron in solution in concentrations toxic to rice.

Low nutrient status

Although acid sulphate soils have sufficient total nitrogen, ammonification under flooded conditions is inefficient.

The average quantity of nitrogen mineralized under aerobic, upland conditions was 5.4% of the total soil nitrogen compared to 7.1% under flooded conditions in acidic soil, at pH 4.5 to 5.5 (Borthakur and Mazumder, 1968). In the soils of the Central Valley, Thailand, $\text{NH}_4\text{-N}$ production during anaerobic incubation is about 3% per season (Kawaguchi and Kyuma, 1969). Addition of lime or phosphate increases N mineralization (Hesse, 1961; Kawaguchi and Kyuma, 1969). Phosphorus deficiency and strong acidity apparently retarded ammonification in acid sulphate soils (Kawaguchi and Kyuma, 1969).

The phosphorus content of acid sulphate soils is low; phosphate is also strongly fixed in these soils. Pham huu Anh et al. (1961) failed to detect any available P with Olsen's method throughout the profile in an acid sulphate soil in Vietnam. In Thailand, phosphorus deficiency in acid sulphate soils was reported by Kanarengsa et al. (1972) and Matsuguchi et al. (1970). Tanaka and Navasero (1966a) found that acid sulphate soils from Vietnam and Malaya had little available phosphorus, plants in pot culture having small amounts. Heavy dressing of phos-

phate eliminated iron toxicity symptoms and resulted in normal growth of the plants.

Moormann (1961) found that 800 kg rock phosphate per hectare failed to give a residual response with rice in the second year in Vietnam. Hesse (1961) and Watt (1969) reported considerable retention of phosphate by fresh mangrove muds, and Watt also reported very low levels of phosphorus in the water of fishponds in acid sulphate soils in Malaysia. Iron and aluminium played an important part in P fixation (Cole and Jackson, 1950; Kittrick and Jackson, 1955; Koshy and Bito-Mutanayagam, 1961; Perkins and King, 1944). This agrees with the work of Tomlinson (1957) who suggested that P was immobilized by iron. Black and Goring (1953) indicated that inorganic P will be immobilized during the decomposition of organic matter containing less than 0.2 per cent organic P. This resulted in low available P in an acid sulphate soil. Potassium may be deficient in some acid sulphate soils but, as in the case of calcium and magnesium, no detailed investigations have been reported (Bloomfield and Coulter, 1973).

Hydrogen sulphide

At the pH values of most flooded soils, most of the H_2S in the soil solution is present as bisulphide ion and undissociated H_2S . Hydrogen sulphide concentrations as low as 0.007 mg/l have been reported to be toxic to rice seedlings in culture solutions (Mitsui et al., 1951). A number of nutritional disorders of rice have been associated with H_2S toxicity in different countries, depending on the timing and the symptoms of the damage (Baba et al., 1964; Tanaka and Yoshida, 1970). Vangnai et al. (1974) gave some indirect evidence for sulphide toxicity in rice on acid sulphate soil. Harmful concentration of H_2S may be present in acid sulphate soils and acid soils low in iron during the first few weeks after flooding (Ayotade, 1977).

2.1.3 Reclamation and improvement

Reclamation measures for lowland rice include prolonged submergence, leaching with seawater or rain water or a succession of these, addition of lime or manganese dioxide or combinations of these.

Submergence

When a acid soil is flooded, the pH rises (Hesse, 1961; IRRI, 1963). The increase in pH is mainly due to reduction of ferric oxides to dissolved Fe^{2+} , a process that consumes acidity (van Breemen and Pons, 1978). If an acid sulphate soil is kept submerged until the pH increases sufficiently, aluminium toxicity is eliminated and iron toxicity minimized (Ponnamperuma, 1964), and rice grows normally.

Farmers in Indonesia, Vietnam and Thailand have evolved systems for cultivating rice on these soils. In Indonesia (Driessen and Ismangun, 1973), Bandjarese farmers of South Kalimantan manage the potential acid sulphate soils by a very shallow tillage to deal with weed growth, leaving the potentially acid sulphate material undisturbed; they use old rice seedlings transplanted several times so that in the final transplanting the seedlings are large enough to cope with toxic elements.

Moormann (1961) reports that the farmers in Vietnam grow rice over quite a proportion of the Mekong delta, on soil with a pH of 2.8 when aerated, by maintaining waterlogged conditions as much as possible.

In Thailand also, van der Kevie (1972) reports that a rice variety tolerant of deep flooding is the major crop on these soils.

The farmers' successful technique of submerging these soils is supported by pot and field experiments in other parts of the world. In Guyana, Cate and Sukhai (1964) used pot experiments to demonstrate the value of prolonged preflooding of toxic soils before planting rice.

Drainage and leaching

The development of acid conditions and the rise in soluble salts in an acid sulphate soil after drainage is caused by pyrite oxidation following air entry. It has been frequently proposed that acid sulphate soil should be drained intensively to leach out these acids and soluble salts. Leaching increases the pH, lowers specific conductance and lowers the concentration of aluminium and other salts, as well as the partial pressure of CO_2 (Cate and Sukhai, 1964; Hesse, 1961; Ponnampetuma et al., 1973). Many laboratory experiments have been reported on the rate of oxidation of pyrite, and on the requirements for leaching of acid sulphates. Richmond et al. (1975) showed that upon drainage, pH decreased and $\text{SO}_4\text{-S}$ increased rapidly when the degree of pore water saturation fell below 0.95. Fleming and Alexander (1961) conducted leaching experiments in the United States and reduced the pyrite content of 2-3% to only 0.34-0.40% in 10 years time. In Malaysia Bloomfield et al. (1968) managed to bring an original pyrite content of 2% down to 0.36% (at 50 cm depth in 5 years time), using tile drains with a 10-60 m spacing at 1 m depth. Experiments in the Medina experimental polder in Senegal (Beye, 1973) where different drainage intensities were imposed, showed the detrimental effects of intensive drainage. Hart et al. (1963) estimated that one field season's drying would oxidize about half the pyrite present. Another laboratory in Sierra Leone (Annual Report, 1959) showed that daily leaching with seawater or fresh water removed half the titrable acidity of the oxidized soils after using five times the weight of soil, the rates of leaching being the same for both fresh water and seawater. After leaching a soil of pH 2.6 with 15 times its weight of water, its lime requirement (to pH 5.2) was lowered from 38 to 8 tons CaCO_3 per hectare per 15 cm. Kivinen (1950) reported an increase in pH from 2.5 to 3.7 when small samples of acid clays were leached with copious quantities of water. It should be kept in mind, however, that the conditions for oxidizing and leaching small, well homogenized samples in the laboratory are very different from those in the field.

A number of one-season trials have been reported. In Sierra Leone, where the excess of rainfall over evaporation in the rainy season may

exceed 1200 mm leaching by rain is an extremely slow process and may take 10 years to complete (Annual Report, 1959).

Experiments on leaching with seawater or brackish water have been reported from Sierra Leone (Hart et al., 1963) and Guyana (Evans and Cate, 1962). Bower and Hardier (1970) found that leaching an acid sulphate soil with seawater removed a large amount of Al, increased pH and exchangeable Na and K, and slightly depressed exchangeable Ca and Mg. It has been suggested that the saline water acts in the same way as a neutral salt solution in the laboratory experiments so that exchangeable aluminium is displaced from the soil by the basic cations in the seawater.

Liming

Acidity can obviously be corrected by liming (Chang and Puh, 1951, McLean et al., 1964; Ponnampetuma, 1960). Lime supplies Ca, removes toxic aluminium by hydrolysis and precipitation and increases the availability of phosphorus (Black, 1968, Coleman et al., 1958, Khallik, 1959, Mehlich, 1946; Ponnampetuma et al., 1973, Pierre, 1938, Struthers and Sieling, 1950, Tisdale and Nelson, 1966). Liming decreases soil acidity and counteracts the poor physical conditions brought about by leaching (Hesse, 1961). Lime added to rice soils under flooded conditions increased mineralization of soil nitrogen and released about 100 per cent more $\text{NH}_4\text{-N}$ from the soil during the first 14 days of waterlogging (Abichandani and Patrick, 1955, 1961). Aslander (1952) found that addition of lime resulted in rapid decomposition of organic matter. Nambiar (1961) attributed this to the stimulation of microbial activity. Another important effect of liming is to increase the availability of most plant nutrients (Truog, 1948). Lime decreases the Fe^{2+} in the soil solution, hence iron toxicity can be alleviated by liming (Ponnampetuma, 1958, 1960; Subramoney and Balakrishmakurup, 1961, Takigima and Kanaganayagan, 1970, Tanaka and Navasero, 1966b). Leaching and liming together has improved pyritic muds (Zuur, 1952, Attanada, 1971). Previous leaching lowers the lime requirement substantially by the removal of acidic substances.

Lime rates of 3 to 6 tons CaCO_3/ha are generally best and several field

and pot experiments indicate that higher applications are even harmful (Pham Huu Anh et al., 1961, Ha, 1970; Park et al., 1971; Yang, 1976; Sombatpanit, 1975; Takahashi et al., 1979). The reasons for the overliming effect are not clear, but it has been attributed to temporary alkali damage (Park et al., 1972) and formation of sparingly soluble calcium phosphate compounds (Sombatpanit and Wangpaiboon, 1973). Application of large amounts of the slower acting wollastonite (calcium silicate) had no overliming effect (Park et al., 1972).

A three-year experiment in Rangsit, Thailand (Suthdhani and Glasewig-gram, not dated) to study the effect of liming on the yield of rice, at three rates of 1875, 3750, and 7500 kg slaked lime per hectare recorded a yield increase from the first year with a tendency of cumulative benefit.

Other treatments

Manganese dioxide retards soil reduction by virtue of the high standard oxidation-reduction potential of the $\text{MnO}_2 - \text{Mn}^{2+}$ system. Manganese dioxide improved the growth and yield of rice in an acid sulphate soil because it depressed the concentration of water-soluble Fe^{2+} and Al^{3+} (Mai thi My Nhung and Ponnampereuma, 1966; Ponnampereuma et al., 1965, 1973). A reclamation study of a kosh soil in Bangladesh (Islam and Shah, 1968) showed that liming and MnO_2 gave the best growth. This result was attributed to (a) the depression of aluminum toxicity and (b) the rise in pH and the accompanying increase in the availability of nutrients.

2.1.4 The need for research to monitor chemical changes and plant performance under various reclamation measures

Many laboratory experiments have determined the rate of oxidation, e.g. acidification and leaching, but very little work has been done in field conditions or on undisturbed cores, which would be the nearest approximation to the field situation. The rates at which the resulting sulphates are leached and the degree of acidity that develops on oxidation

and leaching are obviously of great importance in the improvement of these soils for agriculture.

Field trials and pot experiments indicated that acid sulphate soils can be put into production for lowland rice by leaching, liming, liming plus leaching, application of manganese dioxide or prolonged submergence. Over a large area the use of lime or manganese dioxide is not economically feasible and prolonged submergence may not be possible because of inadequate possibilities for water control. Therefore, a study on the effects of different agronomic and water management methods on these soils is of primary importance. Different packages should be based on hydrological factors, availability of irrigation water, cropping intensity, cropping schedule and present management practices. The physical and chemical changes induced by different management practices should be well monitored.

Objectives:

The objectives of this study are:

1. To study the dynamics of chemical changes in soils with time under different water management and agronomic packages.
2. To find a practical method or methods of reclamation and improvement of acid sulphate soils on the basis of the results under objective 1.

2.2 Materials and methods

2.2.1 Preparation of undisturbed soil cores

Research on acid sulphate soils has largely been of two main types: fundamental laboratory experiments on individual, disturbed soil samples and reclamation trials in the field. The results from the former are not directly transferable to field conditions; the latter generally do not allow for sufficient measurements to determine the rate and extent to which the different processes influence soil conditions and crop growth.

Undisturbed soil cores of large size are desirable for the study of the

dynamics of soil physical and chemical changes in a closely controlled system that is similar to the field situation. Techniques to obtain undisturbed soil cores have been reported by different workers (Bannink et al., 1977, Black and Raines, 1978, Craswell and Castillo, 1979, Mielke, 1973 and Watson and Lees, 1975). These methods are used to collect either small samples or large samples mostly for physical studies, but are not suited for the study of water and solute movement without contamination in a system with several growing plants. For this purpose a lysimeter drum was developed that met the dimensional requirements of the specific studies and could still be handled in the field situation (Le ngoc Sen, 1982a).

Design requirements and construction of the lysimeter drum

The design specifications for a lysimeter containing an undisturbed soil profile should satisfy the following requirements:

- a) The lysimeter drum should be of a size and weight that allows collection of a representative soil profile core in swampy areas.
- b) Samples should be large enough to accommodate several rice hills until maturity to minimize boundary effects and to average out the effects of macrostructural heterogeneities in the rhizosphere on the growth of the rice.
- c) The gross weight of the soil profile core should be small enough to allow transport to the experiment station.
- d) The materials used should be resistant to corrosion and should not contaminate the soil profile core.

Available oil drums were used to construct the lysimeters. Each has an inside diameter of 60 cm and a length of 90 cm (Fig. 2.1). Both ends of the drum were cut out by hammer and cold chisel. The rolled edges of the drum were retained. The reinforcement ribs around the drum wall were filled with two-component plastic putty to straighten the inside wall. Holes were drilled in the drum in different positions along its length for later insertion of perforated PVC drainage pipes, soil moisture sampling filters and tensiometers (Fig. 2.1). These are used to drain the water from the profiles, to monitor solute concentrations and to measure changes in soil moisture tension with time along the soil profile. The holes were sealed temporarily by epoxy-painted pieces

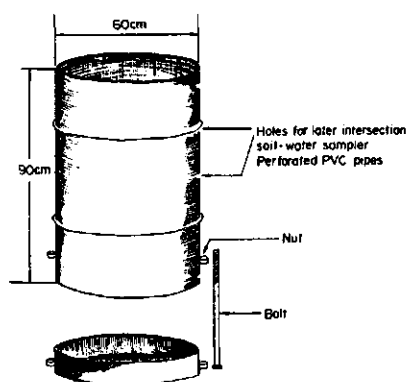


Fig. 2.1 Diagram of a lysimeter.

of sheet metal glued on with two-component epoxy glue. Galvanized iron covers were fabricated for bolting to the bottoms of the drums after collecting the profile cores (Fig. 2.1). The drums and covers were painted with epoxy paint to prevent rust and contamination of the soil.

Collection of soil profile cores

The procedure used in obtaining the samples was to press the drum into the soil in depth increments of 5 to 10 cm by means of a wooden bar placed on top and six to ten persons stepping on it (Fig. 2.2A).

Before each incremental insertion of the drum the soil was trimmed from around the drum to a depth of 5 to 10 cm below the bottom of the cutting edge, so that only a small amount of soil had to be pared away by the cutting edge when the drum was pressed into the soil. The process was continued to the desired depth. The soil below the cutting edge was then cut in a cone shape to prevent fracture of the core while it was dragged out of the profile pit (Fig. 2.2B). One side of the profile pit was cut to a 45° slope. The filled drum was tied with rope, turned 45 degrees (Fig. 2.2C), laid on a wooden pallet and dragged up to the ground surface along the sloping side of the pit. The excess soil material at the bottom was trimmed level with the cutting edge. A galvanized iron cover was then bolted on to close the bottom of the drum (Fig. 2.2D).

If more than one core was to be collected the drums were placed in a row and inserted and excavated in sequence to save digging effort. Experience has shown that ten men can complete collection of 5 cores per day.

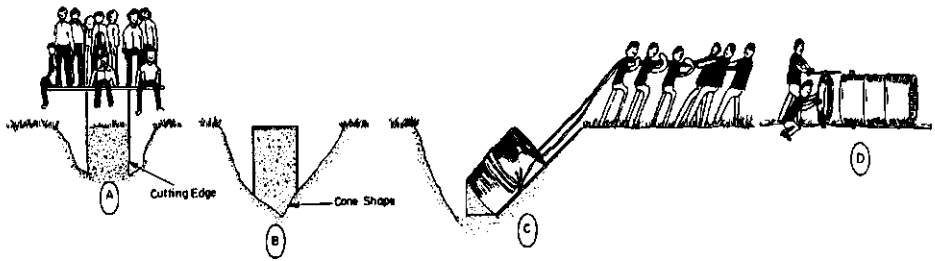


Fig. 2.2 Scheme of field operating procedure to take undisturbed soil cores.

Installation and instrumentation of lysimeters

The joint between bottom cover and drum was sealed with two-component plastic putty. A perforated PVC drainage pipe of 2 cm outside diameter wrapped with nylon mesh (mosquito screen) was installed from the side of the drum at a depth depending on the treatment.

Soil moisture sampling filters, consisting of a Whatman filter tube wrapped with micropore material, were connected with glass tubes and supported by a plastic pipe with the same outside diameter as the available filters (Fig. 2.3). These filter assemblies were installed horizontally at different depths along the profile.

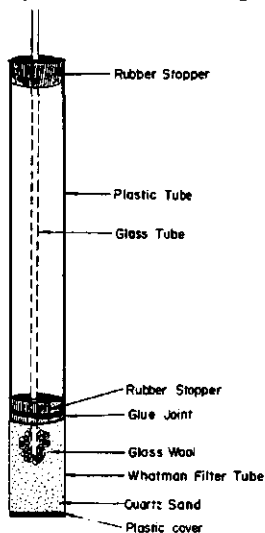


Fig. 2.3 Soil-water sampler components.



Fig. 2.4 Lysimeter cylinders wrapped with fiberglass bla
First rice crop near maturity.



Fig. 2.5 Lysimeter cylinder with vacuum pump and collecting tubes
attached to the soil moisture sampling filters.

Before installing the filter assemblies, a narrow hole was bored out with a soil auger made of plastic to prevent contamination. After installing the assemblies, the joints of the plastic pipes with the lysimeter drum were sealed with two-component epoxy glue. The tensiometers were installed in the same way from the opposite site of the drums. A fiberglass blanket was wrapped around the lysimeter drums to minimize horizontal heat transfer resulting from direct sunlight on one side of the drums (Fig. 2.4). A vacuum pump was used to draw soil solution from the sampling filters into collecting tubes (Fig. 2.5).

Cost and performance

The cost of this lysimeter is about US \$ 60: one third of the cost of fiberglass or PVC pipes of the same size. Forty-eight undisturbed soil profile cores, 80 to 85 cm long, were obtained from different places in the Philippines. Eight cores were used for the primary test and the other forty were used to set up the experiment. Water movement slowed down somewhat after leaching the cores for one month, probably due to closing of the initial gap between the clay soil and the moisture sampling filters and drainage pipes. In all other respects, the performance of the lysimeters was stable over the two-year period of observations, covering three cropping seasons.

2.2.2 Experimental treatments

Two acid sulphate soils from Aparri and Sinacaban, Philippines were used for this study. Information about their profiles is given in Appendix 2.1 and some of the physical and chemical properties are presented in Tables 2.1 and 2.2.

The combination of agronomic and water management packages applied to the cores is shown in Table 2.3. The lysimeters were arranged in four parallel rows 1 m apart, with 10 lysimeters (0.5 m apart) in each row and the treatments were randomly distributed. Each treatment was replicated two times. IR36 rice variety has been used. In treatments 3, 4, 5, 7, 8, 9 and 11 lime was mixed with the upper 20 cm of the soil 20 days before transplanting. N, P, K fertilizers were applied at the

Table 2.1 Some chemical properties of Aparri and Sinacaban acid sulphate soils.

Soil depth (cm)	Chemical properties		EC mS/cm	pyrite (%S)	organic (%)	Total N (%)	CEC (meq/100gr)	Extractable (meq/100 gr)							Fe (%)	Mn (ppm)	P _{total} (ppm)	P _{Olsen} (ppm)
	pH	pH						Na	K	Mg	Ca							
fresh aerated	1:1 extract																	
Aparri																		
0 - 25/30	5.0	4.2	19.1	0.01	7.60	0.50	42.6	21.3	1.3	13.6	7.0	3.6	94	238	1			
25/30 - 40/46	4.2	3.9	26.4	0.08	10.90	0.51	45.6	32.4	1.3	13.0	13.7	2.9	94	250	4			
40/46 - 60	4.3	3.7	29.4	1.10	12.20	0.47	49.0	34.2	1.4	14.1	7.1	1.7	100	205	9			
60 - 90	6.2	3.5	12.8	2.60	13.63	0.32	38.0	17.9	1.3	19.5	9.9	3.3	224	295	2			
Sinacaban																		
0 - 10/15	6.1	4.1	36.5	0.20	5.86	0.31	14.9	23.2	2.2	8.2	6.8	5.3	126	771	5			
10/15 - 20/25	6.4	3.8	42.3	1.60	7.99	0.33	20.3	22.0	1.6	7.3	5.1	5.2	121	772	5			
20/25 - 40	6.4	3.5	44.1	3.10	9.23	0.32	25.8	23.0	0.2	11.5	6.5	5.4	166	603	7			
40 - 70	6.0	3.3	50.1	4.40	11.70	0.39	27.4	37.1	0.1	13.9	8.3	5.0	190	418	3			
70 - 100	6.0	2.9	52.5	3.90	12.30	0.38	29.4	41.3	0.1	18.1	14.2	5.4	223	318	4			

same levels for all treatments. The experiment was carried out according to the following scheme:

- 10 July 1980 - 30 August 1980 : the first leaching period
- 5 September 1980 - 16 November 1980 : the first rice crop
- 16 November 1980 - 30 May 1981 : the soils were kept submerged
with water to wait for soil
moisture equipment
- 17 June 1981 - 30 August 1981 : the soils of the respective
treatments were drained to
subject them to the oxidation
process.
- 1 September 1981 - 30 September 1981: the second leaching period
- 6 October 1982 - 15 December 1981 : the second rice crop
- 15 January 1982 - 1 April 1982 : the third crop

An unexpected typhoon occurred in November 1981 affecting partly the rice yield of the second crop.

Table 2.2 Particle size distribution of different depths along soil profiles of Aparri and Sinacaban acid sulphate soils.

textural analysis		Aparri	
soil depth (cm)	clay (%)	silt (%)	sand (%)
0 - 25/30	53.2	35.7	11.1
25/30 - 40/46	32.2	38.1	29.7
40/46 - 60	15.2	37.1	47.7
60 - 90	10.2	71.0	18.8
		Sinacaban	
0 - 10/15	20.0	58.9	21.1
10/15 - 20/25	9.0	65.6	25.4
20/25 - 40	8.7	49.9	41.4
40 - 70	15.0	35.6	49.4
70 - 100	14.0	36.0	50.0

Table 2.3 Treatment combinations used in the drum experiment.

		<u>Treatment Water management</u>					
		Deep	Shallow	Flushing	Percolation	Mulching	Liming ¹⁾
replicates		Drainage	Drainage				
							0 1 2
1	2	x			x		x
2	2	x					x
3	2	x			x		x
4	2	x					x
5	2	x					x
6	2		x				x
7	2		x				x
8	2			x			x
9	2		x			x	x
10	1			x			x
11	1		x				x

- 1) Deep drainage: drain at 80 cm below surface only applied during leaching periods
 Shallow drainage: drain at 40 cm below surface only applied during leaching periods
 Flushing: renewal of water standing on the surface every 3 days during leaching periods
 Percolation: removal of excess water through the drains during the growing season
 Mulching: application of 5 cm of rice straw during dry season
 Liming, 0: no lime
 1: 1 ton/ha for Aparri soil and 1.25 tons/ha for Sinacaban soil
 2: 2 tons/ha for Aparri soil and 2.5 tons/ha for Sinacaban soil.

Lime was applied 1 week before transplanting rice. During the growing periods, water was maintained 15 cm depth above the soil surface and the drains were blocked.

2.2.3 Analytical methods

The physical and chemical characteristics of the soils were determined according to the following scheme:

1. Textural analysis: pipette method
2. pH: pH meter
3. EC: EC meter with 1:1 extract
4. Sulphate: gravimetric method
5. Soluble and exchangeable aluminium: atomic absorption spectrophotometer
6. Free oxide iron: atomic absorption spectrophotometer
7. Mn^{2+} : atomic absorption spectrophotometer
8. Total phosphorus: Olsen method (Black et al., 1965)
9. Total carbon: Walkey and Black Method (Black et al., 1965)
10. Buffer lime requirement
11. Extractable cations: extraction with ammonium acetate and CEC (Black et al., 1965)
12. Total nitrogen: Kjeldahl method (Black et al., 1965)
13. Pyritic sulphur: (Begheijn et al., 1978)

Surface water, drainage water and the soil solutions along the soil profile were collected weekly for the first cropping season and bi-weekly for the second and third cropping seasons. The pH, EC of surface water and soil solutions were measured directly by pH meter and EC meter, respectively. The soil solutions were acidified with a few drops of 6N HCl to prevent oxidation of Fe^{2+} and Mn^{2+} . Subsequent analysis of the acidified solutions were made. Al, Fe, Ca, Mg, K and Na were determined directly by atomic absorption spectrophotometer.

Observations on the symptoms of deficiencies and toxicities were made on the rice plant during the growing season. Measurements were carried out at weekly intervals on rice plants including plant height, number of tillers, number of panicles, percentage of tillering, percentage of flowering.

After the harvest, grain/panicles and straw weights were determined. The straw was analyzed for N, P, K, Mn, Fe, Al, Ca, Mg.

2.3 Results and discussion

Before starting the experiments, the filters and drainage pipes were installed along the soil profile to collect soil water solutions for monitoring the chemical changes during leaching periods and rice growing seasons. Although the soils were carefully maintained saturated with water before setting up the experiment, some of the lysimeter drums were leaky and pyrite oxidation was taking place. Results therefore yielded some variations among treatments. In the following sections the physical and chemical properties of each soil will be presented and discussed.

2.3.1 The amount of drainage water collected under different water management practices during the first and second leaching periods

Table 2.4 shows the amount of drainage water collected under different water management practices in Aparri and Sinacaban acid sulphate soils during the first and second leaching periods. Both soils have highest amounts of drainage water when deep drainage was imposed. In Sinacaban soil, the amount of drainage water collected during the second leaching period was higher than the first one. In this soil large amounts of

Table 2.4 The amount of drainage water collected under different water management during the first and second leaching periods.

Water management treatment	The amount of drainage water (mm)			
	Aparri		Sinacaban	
	First leaching	Second leaching	First leaching	Second leaching
Flushing	100	30	140	100
Shallow drainage	140	60	200	340 (250)
Deep drainage	210	110	300	450

Value in parenthesis is the amount of drainage water in shallow drainage with mulch treatment.

Table 2.5 Average soil moisture content (by weight) and n-value of different depths along the profile of Aparri and Sinacaban acid sulphate soils at the end of dry season, 1981.

Treatment	Soil depth (cm)		Soil moisture, g per 100 g dry matter					
			Aparri					
	0-10	10-20	20-30	30-40	40-50	50-60	60-70	70-80
1	12.0	40.7	41.4	64.7	91.4	96.9	117.2	-
2	15.3	44.0	61.4	60.3	78.5	73.4	105.9	107.3
3	10.4	27.8	50.9	79.5	79.9	101.0	102.9	103.2
4	24.4	39.4	43.2	52.6	75.2	85.7	103.7	-
5	15.6	38.9	51.3	68.8	70.3	102.6	102.0	109.9
6	14.6	34.6	52.4	63.9	85.3	104.5	123.9	-
7	12.7	34.0	53.5	71.6	79.3	88.8	118.3	-
8	-	-	-	-	-	-	-	-
9	53.2	62.0	65.0	93.7	108.9	-	97.7	-
10	-	-	-	-	-	-	-	-
11	19.9	36.0	47.1	49.7	61.9	75.3	109.1	121.6
Sinacaban								
1	33.9	72.1	91.3	106.9	111.2	120.1	188.6	192.6
2	34.5	59.9	68.0	86.7	113.8	133.6	170.0	-
3	19.0	80.4	92.2	113.2	142.3	137.2	178.2	159.0
4	43.1	71.1	87.1	134.1	197.1	157.4	142.3	175.8
5	45.2	81.5	118.2	141.2	159.3	159.2	175.2	-
6	36.3	82.5	101.9	99.1	107.9	149.2	122.7	101.6
7	21.7	82.2	101.5	123.7	100.8	136.0	163.0	-
8	-	-	-	-	-	-	-	-
9	87.9	94.7	99.2	131.0	144.2	160.0	195.2	-
10	-	-	-	-	-	-	-	-
11	15.2	65.6	71.9	86.9	70.8	90.1	144.1	-
n-value								
Aparri								
1	0.05	0.43	0.44	0.82	1.23	1.59	2.00	-
2	0.10	0.48	0.70	0.75	1.04	1.14	1.78	1.80
3	0.03	0.26	0.56	1.05	1.06	1.67	1.72	1.72
4	0.22	0.41	0.46	0.64	0.99	1.37	1.73	-
5	0.10	0.41	0.57	0.89	0.91	1.70	1.70	1.86
6	0.09	0.35	0.59	0.81	1.14	1.74	2.13	-
7	0.06	0.34	0.60	0.93	1.05	1.43	2.02	-
8	-	-	-	-	-	-	-	-
9	0.60	0.72	0.75	1.27	1.50	-	1.62	-
10	-	-	-	-	-	-	-	-
11	0.16	0.37	0.52	0.59	0.78	1.17	1.84	2.08
Sinacaban								
1	0.51	1.68	2.06	2.49	1.93	2.10	3.47	3.49
2	0.52	1.31	1.42	1.94	1.98	2.37	3.10	-
3	0.11	1.93	2.08	2.66	2.55	2.44	3.27	2.83
4	0.75	1.65	1.95	3.24	3.64	2.85	2.55	3.16
5	0.81	1.96	2.80	3.43	2.88	2.88	3.20	-
6	0.57	2.00	2.35	2.28	1.86	2.68	2.16	1.70
7	0.18	1.99	2.34	2.96	1.72	2.42	2.96	-
8	-	-	-	-	-	-	-	-
9	1.93	2.36	2.28	3.16	2.58	2.90	3.60	-
10	-	-	-	-	-	-	-	-
11	0.05	1.48	1.53	1.94	1.12	1.50	2.58	-

acidity developed during the oxidation process, which required a large amount of water to leach out the acidity and toxic elements.

During the cropping season, the amount of percolation water were 60 and 140 mm for Aparri and Sinacaban, respectively.

2.3.2 Average soil moisture content (g per 100 g dry matter) and n-value of different depths of Aparri and Sinacaban soils at the end of dry season, 1981

Irrespective to soils and water management practices, the soil moisture content increases with depth (Table 2.5). There were large differences in soil moisture content between treatments. In both soils, the highest soil moisture contents were observed in shallow drainage with mulch treatments.

The n-values of different layers in the soil profiles were calculated using formulae developed by Pons and Zonneveld (1965). In Aparri soil n-values at 10-20 cm depth in both the shallow (without mulch) and deep drainage treatments were less than 0.4 (Table 2.5). The shallow drainage treatments with mulch reduced the water loss by evaporation, resulting in higher n-value. Higher n-values were observed in the lower layers of different treatments. In Sinacaban soil, n-values were about two times higher than those of Aparri soils. At the 10-20 cm depths, n-values were about 0.70, whereas n-values greater than 2.0 were found in the lower layers. Similar to Aparri soil, the shallow drainage treatments with mulch produced higher n-values.

2.3.3 Chemical properties of the soil solution of Aparri and Sinacaban acid sulphate soils during the first leaching period and the first crop

2.3.3.1 Aparri soil

In this soil, the initial pH-values were nearly all above 4.0. During the leaching period, the pH value of all treatments increased by about 0.3 unit, except in treatments 10 and 11 (Table 2.6). When the soil was

Table 2.6 pH and EC values of the soil solution at 20 cm below soil surface of Aparri soil in the first leaching period and during the first rice crop.

Treatment	pH											
	First leaching period					First crop						
	Start			End		Average	After transplanting		2 weeks before harvest			
	Rep ₁	Rep ₂	Average	Rep ₁	Rep ₂		Rep ₁	Rep ₂	Rep ₁	Rep ₂	Average	
1	6.0	4.2	5.1	6.0	4.6	5.3	6.0	4.6	5.3	6.4	4.7	5.6
2	4.2	5.8	5.0	4.6	6.0	5.3	4.6	6.0	5.3	4.8	6.5	5.7
3	4.3	4.6	4.4	4.6	5.0	4.8	4.6	5.0	4.8	4.5	5.8	5.2
4	4.9	5.5	5.2	5.1	6.0	5.5	5.1	6.0	5.5	5.4	6.0	5.7
5	4.2	4.6	4.4	4.3	4.9	4.6	4.7	4.9	4.8	5.9	6.0	5.7
6	4.1	4.0	4.1	4.7	4.6	4.6	4.7	4.7	4.7	5.4	5.8	5.6
7	5.0	4.4	4.7	5.2	4.9	5.0	5.2	5.0	5.1	6.5	5.2	5.8
8	4.3	4.4	4.4	4.7	4.9	4.8	4.7	4.9	4.8	5.1	6.0	5.6
9	4.5	6.0	5.2	4.5	6.2	5.3	6.2	4.5	5.3	7.0	4.6	5.8
10	4.0	-	4.0	4.3	-	4.3	4.3	-	4.3	4.4	-	4.4
11	3.6	-	3.6	3.6	-	3.6	3.6	-	3.6	5.8	-	5.8
EC (mS/cm)												
1	4.5	13.6	18.1	1.8	5.4	3.6	1.3	5.0	3.2	1.7	4.4	3.1
2	8.1	13.2	10.6	5.8	3.0	4.4	5.8	3.7	4.8	5.9	4.8	5.4
3	18.9	14.8	16.7	5.5	3.8	4.6	6.0	3.7	4.8	6.1	3.6	4.9
4	6.7	8.2	7.5	4.2	6.4	5.3	4.9	6.0	5.5	5.1	6.2	5.6
5	10.4	9.6	10.0	2.1	3.7	2.9	2.6	3.6	3.1	2.9	3.5	3.2
6	12.9	16.4	14.6	12.4	8.9	10.6	11.3	8.8	10.0	10.4	7.5	8.9
7	6.7	12.9	9.8	3.3	3.5	3.4	3.0	3.6	3.3	3.7	3.2	3.5
8	11.0	13.5	12.2	8.9	10.8	9.9	8.7	9.2	8.9	9.7	10.2	10.0
9	11.0	10.0	10.5	7.2	3.2	5.2	7.2	8.2	7.5	3.4	3.9	3.7
10	16.2	-	16.1	5.7	-	5.7	5.4	-	5.4	5.8	-	5.8
11	16.1	-	16.1	4.9	-	4.9	5.0	-	5.0	4.8	-	4.8

Table 2.7 The pH and EC values of the soil solution at 20 cm below soil surface of Sinacaban soil in the first leaching period and during the first rice crop.

Treatment	First leaching period				pH		First crop			
	Start		End		Average	Rep ₁	After transplanting		2 weeks before harvest	
	Rep ₁	Rep ₂	Average	Rep ₁	Rep ₂	Average	Rep ₁	Rep ₂	Rep ₁	Rep ₂
1	3.8	4.2	4.0	5.0	5.6	5.3	5.0	5.6	6.4	6.3
2	3.1	3.7	3.4	4.0	4.2	4.1	4.8	4.2	6.0	5.6
3	3.1	3.5	3.3	3.7	3.8	3.8	4.4	3.9	6.2	6.0
4	3.8	3.4	3.6	5.0	4.2	4.6	5.0	4.2	7.0	6.7
5	3.8	3.5	3.6	5.0	3.8	4.4	5.8	4.0	6.40	6.8
6	4.0	5.2	4.6	4.7	5.3	5.0	4.7	5.3	6.6	6.6
7	3.7	3.8	3.8	4.3	4.7	4.5	4.3	4.7	6.0	5.8
8	3.9	3.5	3.7	3.9	3.5	3.7	4.6	3.5	6.4	5.0
9	4.6	4.1	4.3	5.6	4.7	5.1	5.6	4.8	7.0	6.0
10	4.0	-	4.0	4.2	-	4.2	4.3	-	4.3	4.3
11	3.2	-	3.2	4.4	-	4.4	4.4	-	6.2	5.3
EC (mS/cm)										
1	24.8	30.2	27.5	9.4	7.8	8.6	7.6	7.2	7.3	7.0
2	19.4	14.3	16.1	5.7	4.7	5.2	4.6	5.0	4.1	4.5
3	23.2	21.4	22.3	3.4	2.3	2.9	3.4	2.8	3.1	2.2
4	14.4	23.1	18.8	3.2	3.6	3.4	4.1	3.7	3.9	2.5
5	7.8	22.3	15.0	1.2	2.5	1.9	1.8	3.3	2.0	2.2
6	26.4	30.7	28.6	7.0	7.1	7.1	7.3	7.6	7.6	8.3
7	13.2	20.8	17.0	2.2	7.2	4.7	3.1	7.8	3.6	7.4
8	20.4	32.2	26.3	11.2	18.4	14.8	11.5	18.0	12.2	17.0
9	15.2	29.6	22.4	3.0	5.0	4.0	3.0	5.2	3.0	5.7
10	31.2	-	31.2	20.1	-	20.1	20.4	-	21.8	-
11	26.5	-	26.5	5.3	-	5.3	5.8	-	6.2	-

flooded with water during the crop growing period, pH values of all treatments increased by about 0.8 unit (Table 2.6). Imposing water management practices to the soil, a considerable amount of salt was leached out or flushed away, resulting in a electrical conductivity drop of all treatments to about 4.5 except with treatments 6 and 9 (Table 2.6). There was only a slight change in EC value during the first crop. The Fe^{2+} concentration in the solution at 20 cm depth below the soil surface remained below 100 ppm during the cropping season.

2.3.3.2 Sinacaban soil

The Sinacaban soil was more acid, with initial pH values below 4.0 and often below 3.5. Similar to Aparri soil, pH values of all treatments increased when water management was imposed and during the crop growing season (Table 2.7). In both shallow and deep drainage treatments, EC values decreased substantially values whereas in the flushing treatments (8 and 10) EC values remained high during this period (Table 2.7). There was little change in EC values of different treatments during the growing period. The Fe^{2+} concentration at 20 cm depth was 700, 1000 and 2000 ppm for one replicate of treatments 6, 7 and 8 respectively. About 300 ppm of Fe^{2+} were observed at 20 cm depth in the other treatments.

2.3.4 Chemical properties of the soil solutions of Aparri and Sinacaban acid sulphate soils during the second leaching period, second and third rice crops

2.3.4.1 Aparri soil

Table 2.8 shows the average pH values over the profile during the second and third crops. There was no marked difference in pH among treatments. The movement of oxygen to the lower layers, needed for pyrite oxidation, was hindered by the high percentage of clay in the surface soil (Table 2.2) and the absence of cracks. Even imposing deep drainage to this soil, pH values in all layers remained higher than 4.0

Table 2.8 Average pH values of Aparri soil in the profile and during the second and third crops.

Treatment	pH		Average
	Rep ₁	Rep ₂	
1	5.9	5.8	5.9
2	5.3	6.0	5.7
3	6.1	5.7	5.9
4	6.4	5.5	6.0
5	6.3	6.0	6.2
6	5.4	5.7	5.6
7	5.7	5.6	5.7
8	6.0	5.8	5.9
9	5.8	5.9	5.9
10	6.1	-	6.1
11	6.0	6.0	6.0

Table 2.9 Average pH values during the second and third crops at different soil depths in Aparri soil.

Treatment	soil	pH				
	depths (cm)	0	20	40	60	80
1		6.8	6.2	6.5	5.1	5.5
2		6.8	5.4	5.2	5.0	5.6
3		7.6	6.4	4.7	4.4	5.7
4		7.5	6.1	4.5	5.3	5.7
5		7.2	6.7	5.3	5.3	5.9
6		6.8	5.7	5.9	4.2	5.9
7		7.5	6.0	6.5	4.4	4.3
8		7.9	6.6	5.0	4.3	4.2
9		7.7	6.2	4.5	6.4	5.0
10		7.4	6.6	4.5	6.4	5.0
11		7.2	6.6	5.8	4.9	4.5

(Table 2.9). The Aparri soil, therefore, will not cause severe problems upon reclamation.

2.3.4.2 Sinacaban soil

* Effects of lime on the chemical properties of deep drainage treatments.

-pH

The changes of pH values in the soil solution of surface soil (20 cm below the surface) during the second leaching period, the second and third crops are shown in Fig. 2.6. Even in the treatments with lime, the initial pH values were again well below 4.0. Regardless of lime levels, pH values increased as drainage proceeded. The overall trends in the changes of the pH values of the soil solution appear to be similar (Fig. 2.6). There was little influence of lime on the pH of the soil solution during the second crop, because the acidity remained high during this period. The influence of liming, however, is illustrated by the frequency of occurrence of pH values below 3.5 in the surface water and in the soil solution at a depth of 20 cm during the second crop (Fig. 2.7). The frequency of pH below 3.5 in the surface water was 100 and 50 percent at application of 1.25 and 2.5 tons lime per ha, respectively whereas a lower percentage was observed at 20 cm depth. During the third crop, and at both lime levels, the pH values of the soil solution at 20 cm depth increase to nearly 6 (Fig. 2.6). The lower pH values after application of 2.5 tons lime/ha could be explained by the upward diffusion of acidity from greater depth.

-EC

The electrical conductivity in the 20 cm depth of 1.25 tons of lime/ha became lowest during the leaching period (Fig. 2.8). Under the flooded conditions during the second crop the electrical conductivity increases, regardless of lime levels. The differences in EC values directly after leaching remained during the second and the third rice crops. The high EC values of the treatments with 2.5 tons of lime/ha

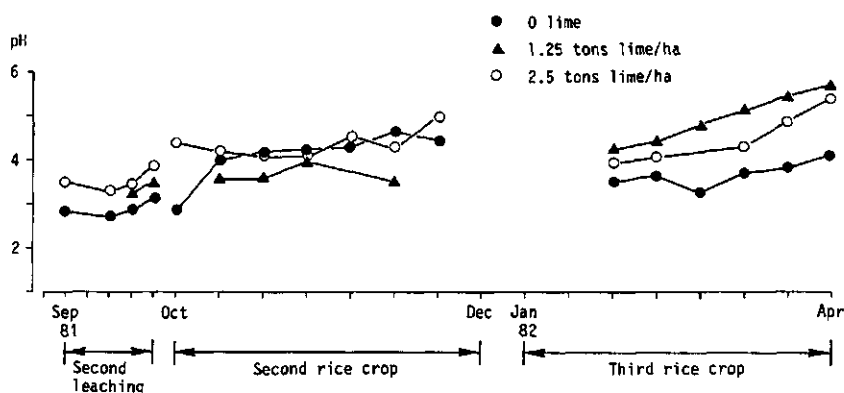


Fig. 2.6 The changes of the pH values in the soil solution at 20 cm depth of Sinacaban acid sulphate soil during the second leaching period and the second and third crops (treatments: deep drainage, three lime levels).

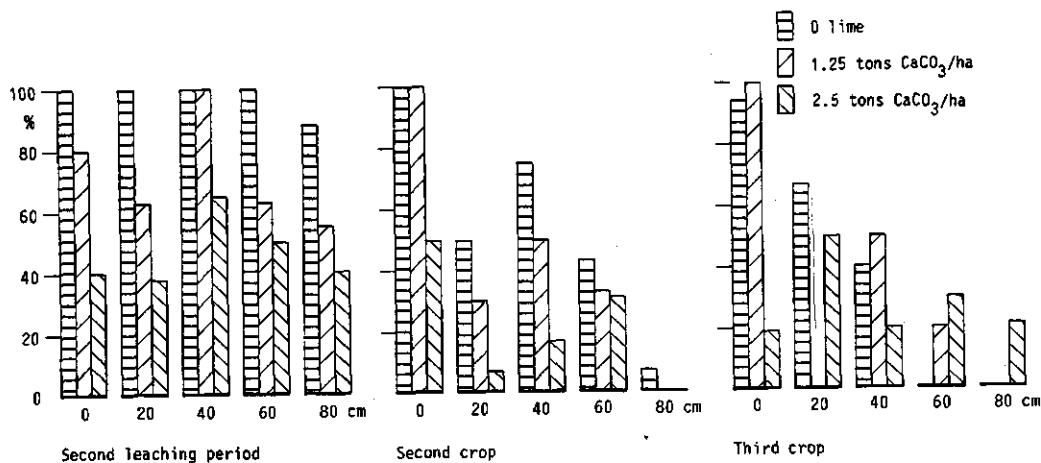


Fig. 2.7 Frequency of occurrence of the pH of the soil solution below 3.5 at different depths in the Sinacaban acid sulphate soil during the second leaching period and the second and third crops (treatments: deep drainage, three lime levels).

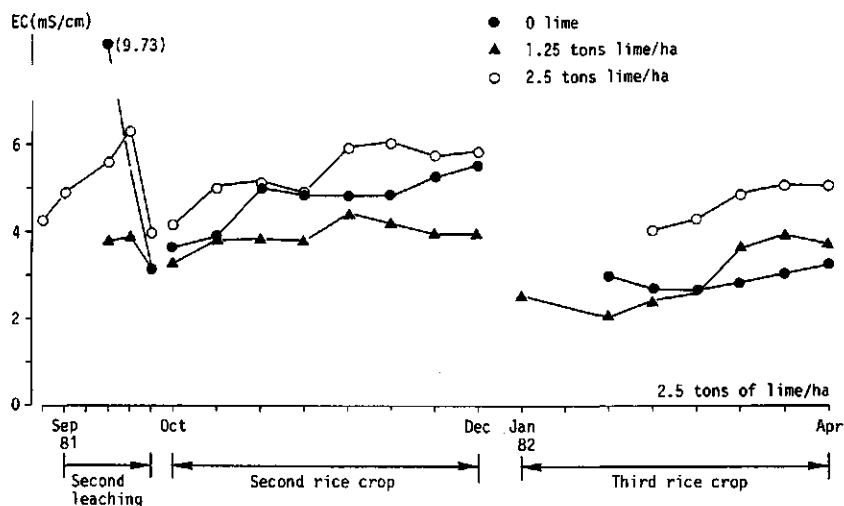


Fig. 2.8 The changes of EC values in the soil solution at 20 cm depth of Sinacaban acid sulphate soil during the second leaching period and the second and third crops (treatments: deep drainage, three lime levels).

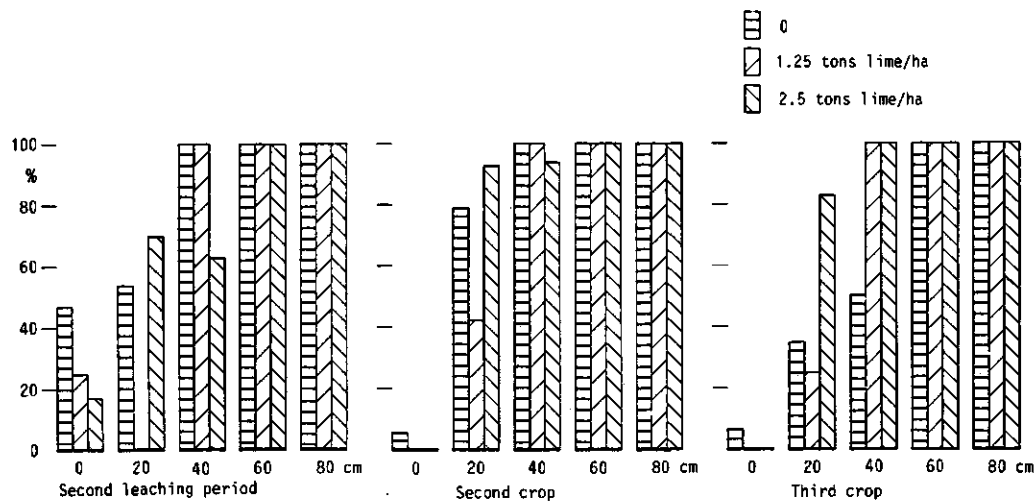


Fig. 2.9 Frequency of occurrence of the EC values of soil solution above 4.0 mS/cm at different depths in the Sinacaban acid sulphate soil during the second leaching period and the second and third crops (treatments: deep drainage, three lime levels).

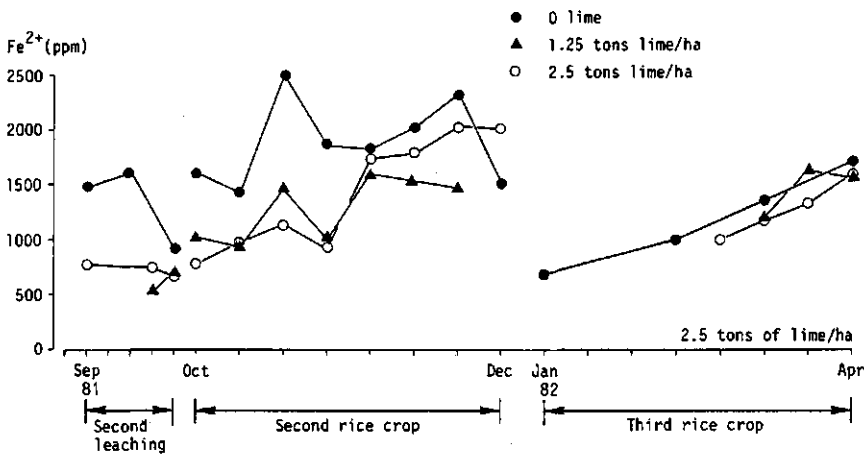


Fig. 2.10 The changes of iron concentrations in the soil solutions at 20 cm depth of Sinacaban acid sulphate soil during the second leaching period and the second and third crops (treatments: deep drainage, three lime levels).

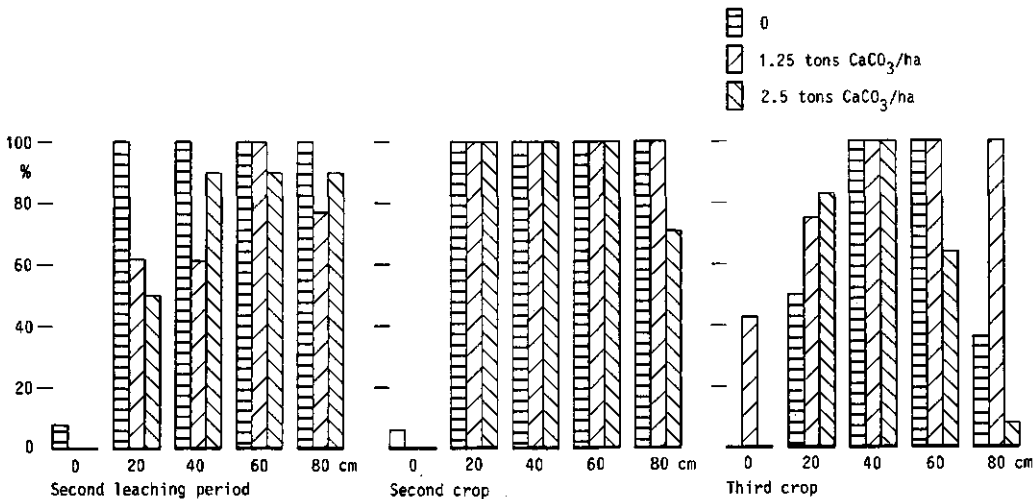


Fig. 2.11 Frequency of occurrence of Fe²⁺ concentrations in the soil solution above 500 ppm at different depths in Sinacaban acid sulphate soil during the second leaching period and the second and third crops (treatments: deep drainage, three lime levels).

were due to high initial EC values in the soil profile (Fig. 2.9). High salinity gradients resulted in upward movement of ions by diffusion.

-Fe²⁺

Lime markedly decreased the Fe²⁺ concentration in the soil solution at 20 cm depth, especially during the second leaching and the second rice crop (Fig. 2.10). There was no marked difference in Fe²⁺ concentration between treatments with 1.25 and 2.5 tons of lime/ha. During the second crop, the Fe²⁺ concentration increases with proceeding duration of submergence, with soluble iron levels reaching over 2000 ppm for the no lime treatment (Fig. 2.10). Even though the Fe²⁺ contents were reduced by liming, they were always higher than the toxic levels (500 mg/l soluble Fe²⁺) as reported by Mai thi My Nhung Ponnamparuma, 1966 (Fig. 2.11), except near the soil surface.

-Aluminium

Directly after the leaching period, the aluminium concentration in the soil solution at 20 cm depth was about 40 ppm at all three lime levels (Fig. 2.12). During the second rice crop, lime depressed the aluminium concentration. The aluminium concentration of the treatments with 2.5 tons of lime/ha was about 40% lower than no lime treatments during the second crop (Fig. 2.12). As a general trend, the aluminium concentration decreased with longer duration of submergence (Fig. 2.13). During the third rice crop, a further reduction in soluble Al occurred.

* Effects of different water management practices on chemical properties of Sinacaban soil when no lime was applied

-pH

Fig. 2.14 shows the changes of pH in the soil solution at 20 cm depth during the leaching period, and the second and third rice crops. The highest pH values were observed in flushing treatments (above 7). There were only little differences in pH values between different drainage treatments (Fig. 2.14), during the second crop, whereas marked differences in pH values were observed during the third crop, with deep drainage treatment without percolation producing the lowest pH values.

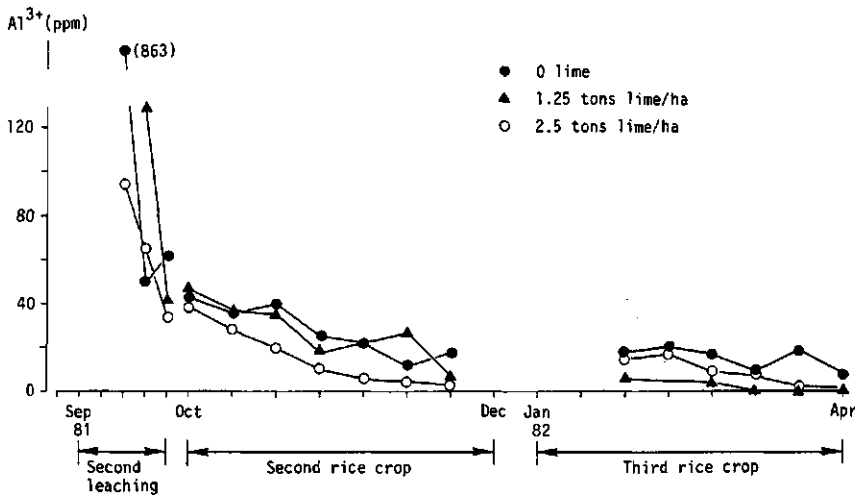


Fig. 2.12 The changes of the aluminium concentrations in the soil solution at 20 cm depth of Sinacaban acid sulphate soil during the second leaching period and the second and third crops (treatments: deep drainage, three lime levels).

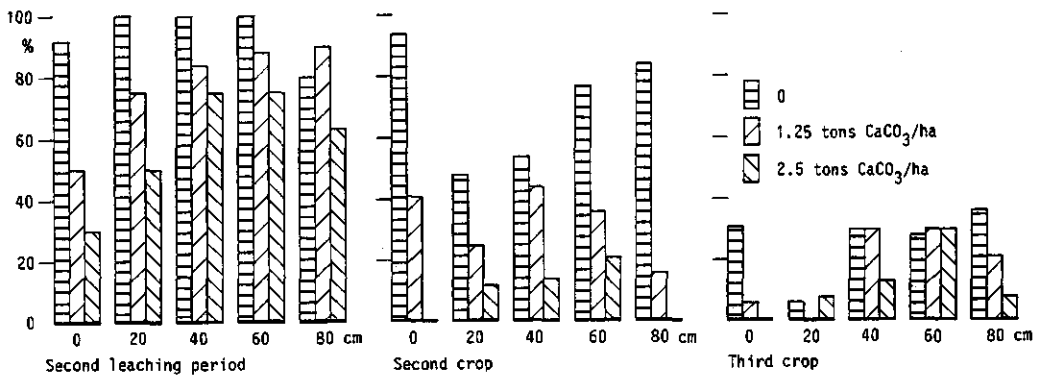


Fig. 2.13 Frequency of occurrence of Al^{3+} concentrations in the soil solution above 40 ppm at different depths in Sinacaban acid sulphate soil during the second leaching period and the second and third crops (treatments: deep drainage, three lime levels).

This can be explained by a lesser pyrite oxidation with shallow drainage as compared to deep drainage. Percolation helped to remove some acidity in the soil profile, resulting in higher pH values.

Regardless of water management, pH values gradually increased by flooding. The highest frequencies of pH in the soil solution below 3.5, at different soil depths, were found in deep drainage treatments without percolation (Fig. 2.15).

-EC

An appreciable amount of salts were leached out from the profiles in both shallow and deep drainage treatments. EC values of these treatments at 20 cm depth were about 4 mS/cm as compared to 9 mS/cm for flushing treatments at the start of the second crop (Fig. 2.16). There was no marked change in EC values during the second crop. During the third crop, higher EC values of the deep drainage treatment with percolation - as compared with the other treatments - may be due to the upward movement of salt by diffusion from lower layers (Fig. 2.16). This was confirmed by the higher frequency of occurrence of high values EC at 40 cm depth (Fig. 2.17). The EC values of the lower depths remained high (Fig. 2.17).

-Fe²⁺

When the soil is kept continuously submerged (flushing treatments), the Fe²⁺ concentration remains very low (Fig. 2.18). The deep drainage treatments with percolation are taking away a large amount of iron in the solution as compared to those without percolation. Shallow drainage resulted in lower iron concentrations in the soil solution because of less oxidation products formed and subsequently less Fe²⁺ formed during the reduction process.

In general, the iron concentration reached its highest peak values after 3 months of submergence during the second crop (Fig. 2.18). A similar trend was observed during the third crop.

As the duration of submergence proceeds, the frequency of occurrence of Fe²⁺ in the soil solution above 500 ppm became less at all depths in the profile (Fig. 2.19).

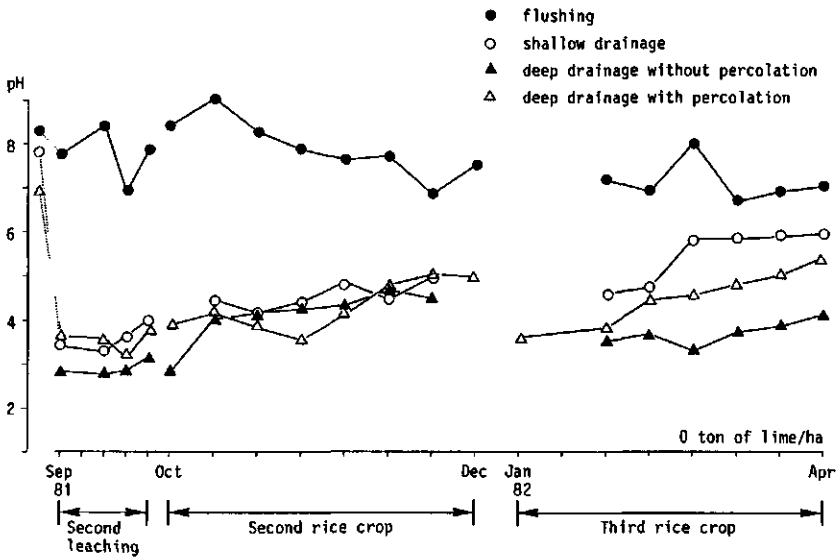


Fig. 2.14 The changes of the pH values in the soil solution at 20 cm depth of Sinacaban acid sulphate soil during the second leaching period and the second and third crops (treatments: 0 t/ha of lime, all water management practices).

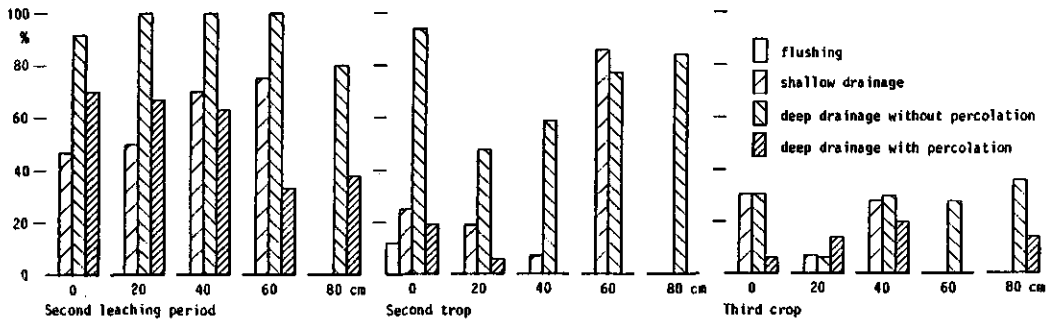


Fig. 2.15 Frequency of occurrence of pH values of soil solution below 3.5 at different depths in Sinacaban acid sulphate soil during the second leaching period and the second and third crops (treatments: 0 t/ha of lime, all water management practices).

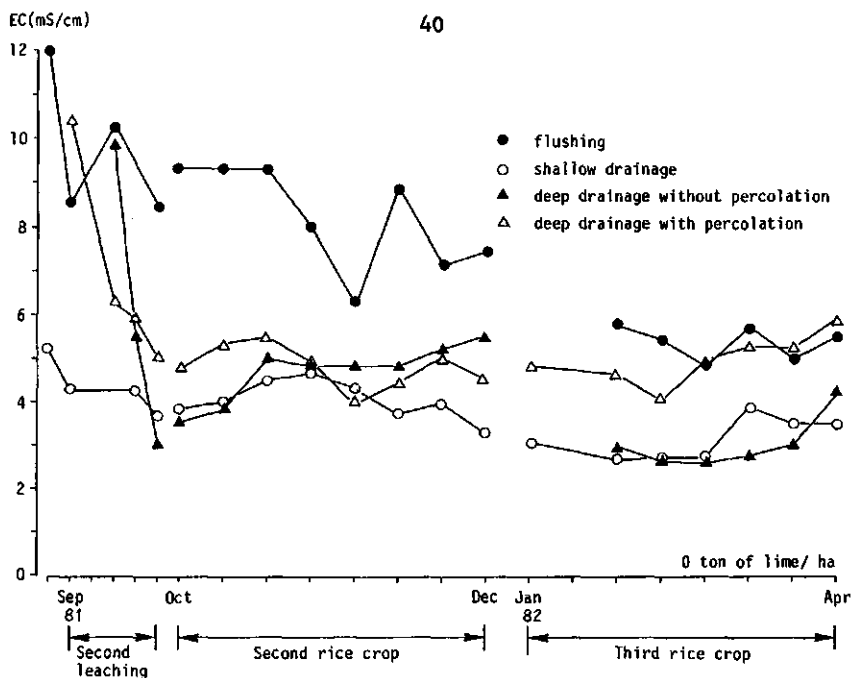


Fig. 2.16 The changes of EC values in the soil solution at 20 cm depth of Sinacaban acid sulphate soil during the second leaching period and the second and third crops (treatments: 0 t/ha of lime, all water management practices).

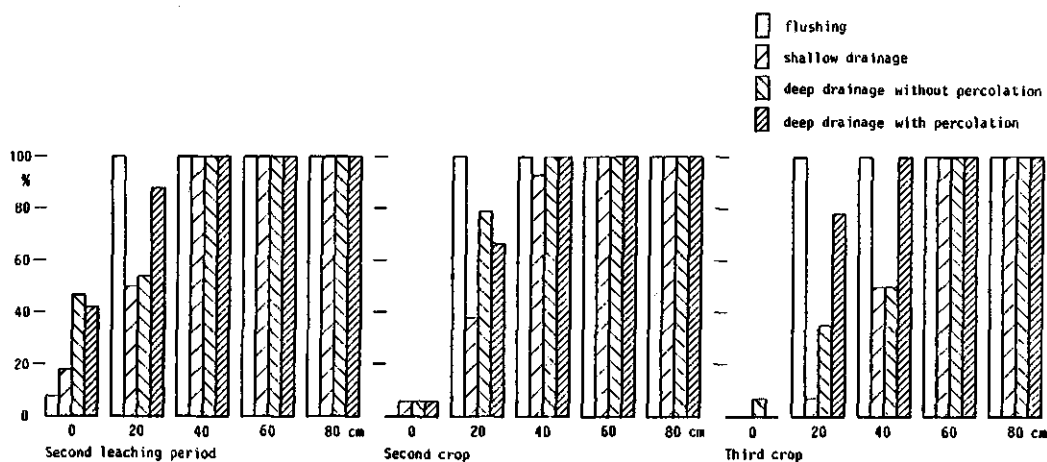


Fig. 2.17 Frequency of occurrence of EC values of the soil solution above 4.0 at different depths in Sinacaban acid sulphate soil during the leaching period and the second and third crops (treatments: 0 t/ha of lime, all watermanagement practices).

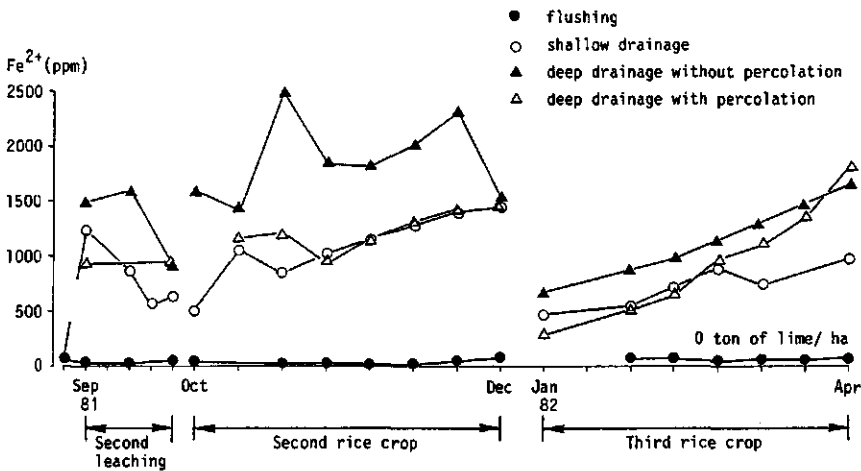


Fig. 2.18 The changes of the iron concentrations in the soil solution at 20 cm depth of Sinacaban acid sulphate soil during the second leaching period and the second and third crops (treatments: 0 t/ha of lime, all water management practices).

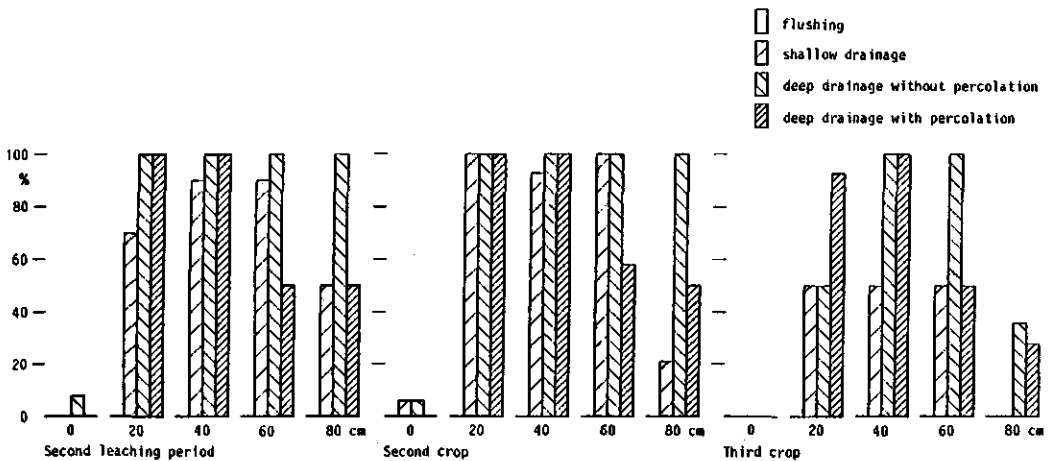


Fig. 2.19 Frequency of occurrence of Fe^{2+} concentrations in the soil solution above 500 ppm at different depths in Sinacaban acid sulphate soil during the second leaching period and the second and third crops (treatments: 0 t/ha of lime, all water management practices).

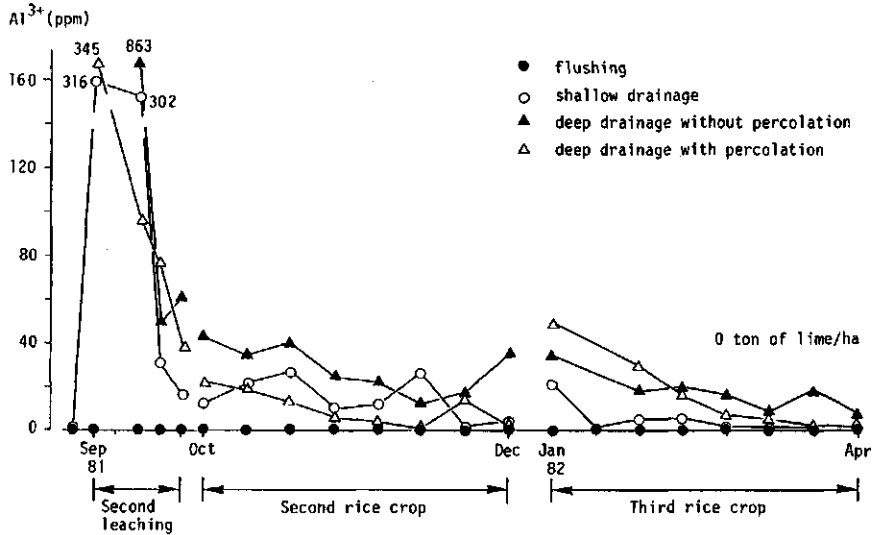


Fig. 2.20 The changes of the aluminium concentrations in the soil solution at 20 cm depth of Sinacaban acid sulphate soil during the second leaching period and the second and third crops (treatments: 0 t/ha of lime, all water management practices).

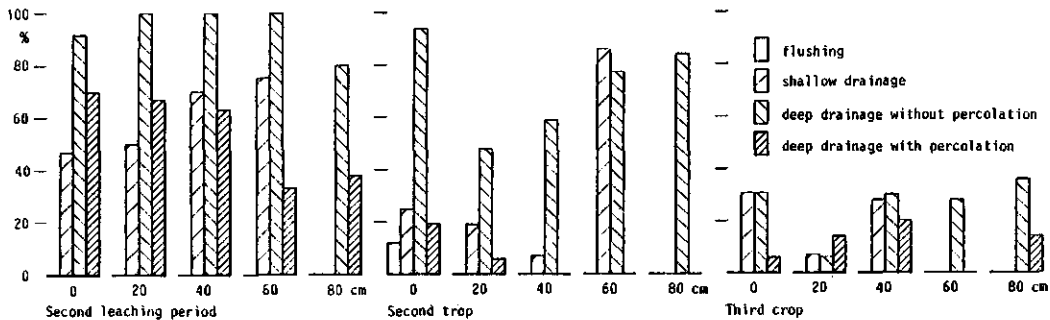


Fig. 2.21 Frequency of occurrence of Al concentrations in the soil solution above 40 ppm at different depths in Sinacaban acid sulphate soil during the second leaching period and the second and third crops (treatments: 0 t/ha of lime, all water management practices).

-Al³⁺

The aluminium concentration in the soil solution of the upper soil layers decreased considerably when drainage treatments were imposed (Fig. 2.20). Shallow drainage resulted in relatively low aluminium concentrations during the second crop and especially during the third crop. During both crop growing periods deep drainage treatments with percolation produced lower aluminium concentrations as compared to those without drainage (Fig. 2.20). This may be explained by the removal of Al-ions by the percolation.

The aluminium concentrations in the soil solution tended to decrease during the crop growing periods.

Because of continuous submergence, a negligible amount of aluminium was found in the flushing treatments. Fig. 2.21 shows the frequency of occurrence of Al concentrations in the soil solution above 40 ppm at different depths during the leaching period and the second and third crops. As the soil underwent reduction for a longer period, the frequency of occurrence of Al concentrations above 40 ppm became less.

* Effects of different water management practices at 2.5 tons/ha of lime application on the chemical properties of Sinacaban soil

-pH

As can be expected, the pH patterns of different water management practices after application of 2.5 tons lime/ha were similar to those without lime, as discussed in the preceding section.

For both shallow and deep drainage treatments, a considerable amount of acidity was removed from the soil profile and the pH values rose 1 unit higher than the initial values of 3.0 (Fig. 2.22). During the second crop, the pH values of the treatments of deep drainage with and without percolation remained low (about 4), whereas the pH values of the shallow drainage treatment gradually increased and reached a peak value of 5.8 at the end of cropping season. The pH values of the flushing treatments showed little variation and fluctuated around 7. The unexpected low pH values of the treatment of deep drainage with percolation as compared to those without percolation during the second crop, may be due to soil variability and the higher acidity in the subsoil layers

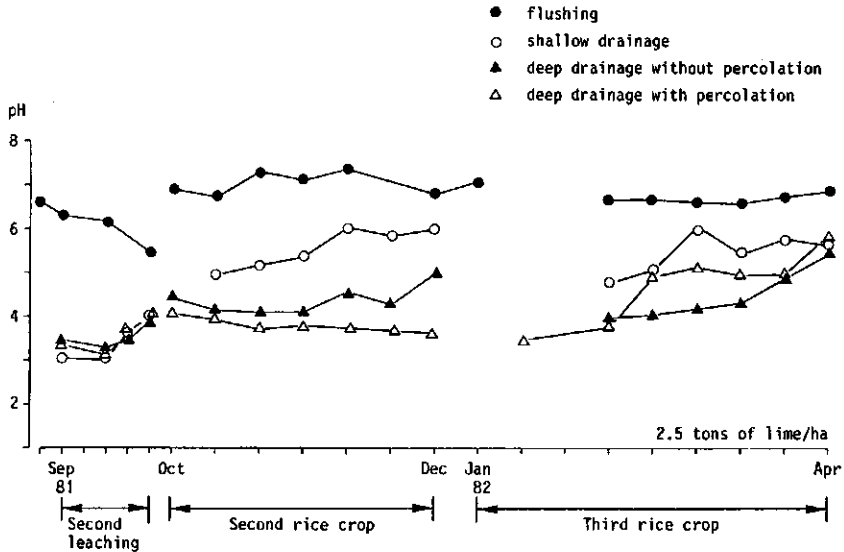


Fig. 2.22 The changes of the pH values of the soil solutions at 20 cm depth of Sinacaban acid sulphate soil during the leaching period and the second and third crops (treatments: 2.5 t/ha of lime, all water management practices).

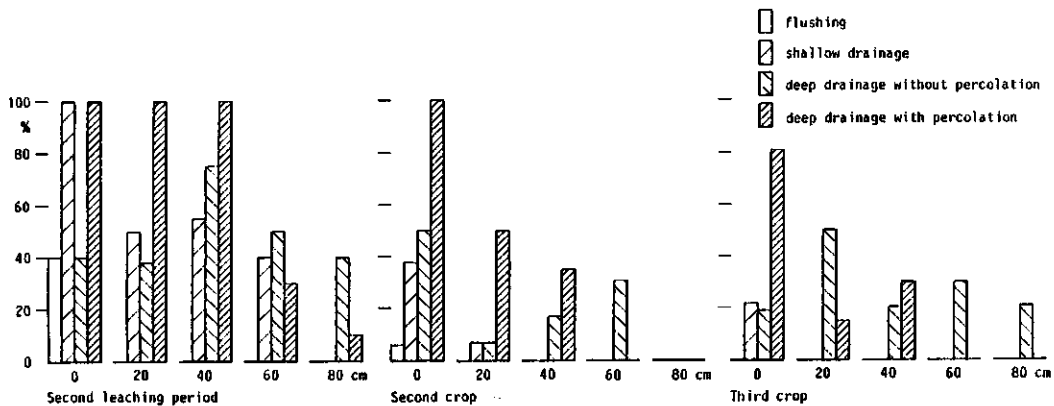


Fig. 2.23 Frequency of occurrence of pH values of the soil solution below 3.5 at different depths in Sinacaban acid sulphate soil during the second leaching period and the second and third crops (treatments: 2.5 t/ha of lime, all water management practices).

which is also reflected in higher frequency of occurrence of pH values less than 3.5 (Fig. 2.23). Except flushing treatments, the pH of drainage treatments increased with prolonged duration of flooding during the third crop (Fig. 2.22). With shallow drainage the peak pH value was earlier reached than with the deep drainage treatments. The reduction processes were obviously retarded in the deep drainage treatments.

-EC

The electrical conductivity of different water management treatments during the leaching period, and the second and third crops is shown in Fig. 2.24. The trends are similar to those observed in the "no lime" treatments. During the leaching period, salts were leached out by drainage resulting in EC values dropping to less than 4 mS/cm in both the shallow and the deep drainage treatments. Higher EC values in the deep drainage treatments during the second crop may be associated with the upward movement of salts from lower layers. This is reflected by the very high frequency of occurrence of EC values above 4 mS/cm (100 percent) in the lower depths of the profile (Fig. 2.25). No difference was found in EC values of the shallow drainage and the flushing treatments during the third crop.

The flushing treatment had low EC values during the entire period. This is probably due to an initial low salt content in the samples taken.

-Fe²⁺

The overall trends of the Fe²⁺ concentration in the soil solution were similar to the "no lime" case. Differences were observed between the shallow and the deep drainage treatments during the second crop (Fig. 2.26). In the shallow drainage treatments, iron reached a peak value of 1500 ppm after two months of flooding, whereas in deep drainage treatments peak values of iron of 2300 ppm occurred near the end of the cropping season. The iron concentration remains low in flushing treatments. During the third crop, the iron concentration in both shallow and deep drainage treatments increased gradually and reached their highest values one month before harvest.

No difference in frequency of occurrence of iron above 500 ppm at 20, 40, 60 and 80 cm depths was found in the shallow and deep drainage

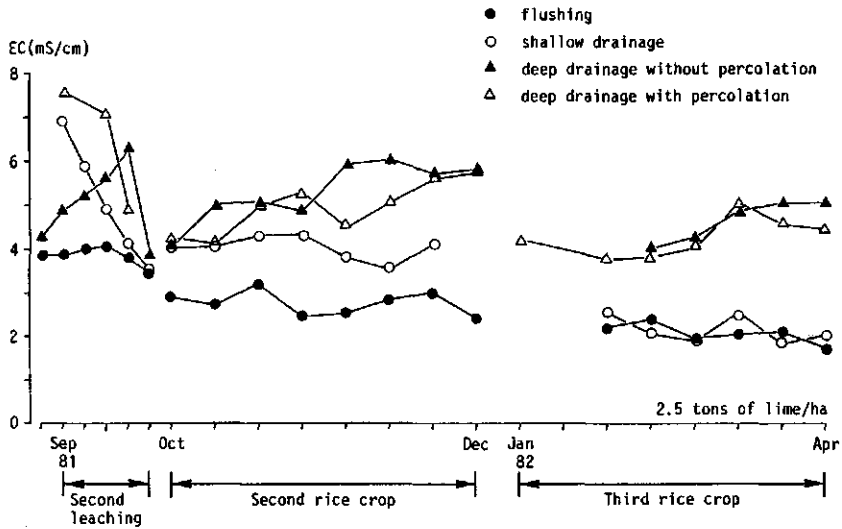


Fig. 2.24 The changes of EC values in the soil solution at 20 cm depth of Sinacaban acid sulphate soil during the second leaching period and the second and third crops (treatment: 2.5 t/ha of lime, all water management practices).

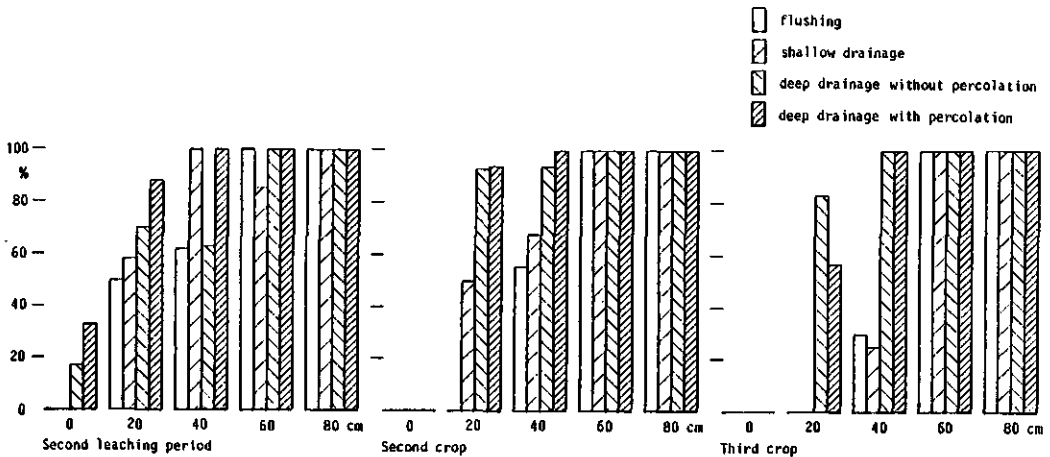


Fig. 2.25 Frequency of occurrence of EC values in the soil solution above 4.0 at different depths in Sinacaban acid sulphate soil during the second leaching period and the second and third crops (treatments: 2.5 t/ha of lime, all water management practices).

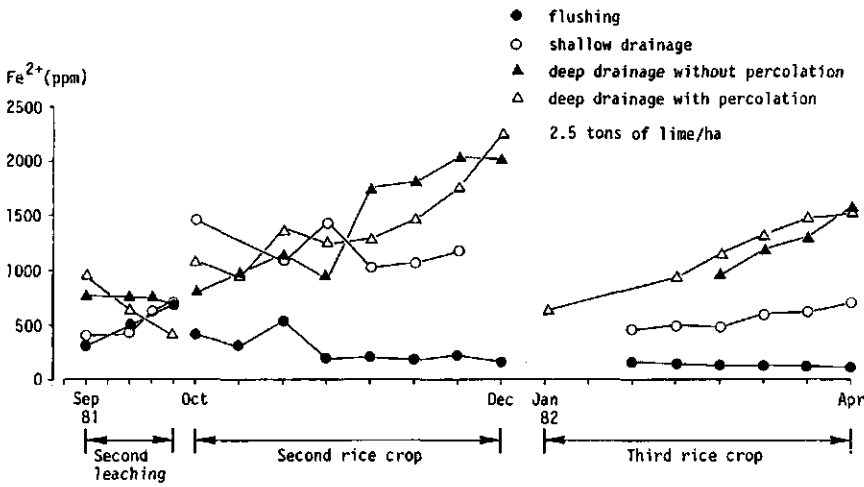


Fig. 2.26 The changes of the iron concentrations in the soil solution at 20 cm depth of Sinacaban acid sulphate soil during the second leaching period and the second and third crops (treatments: 2.5 t/ha of lime, all water management prac-

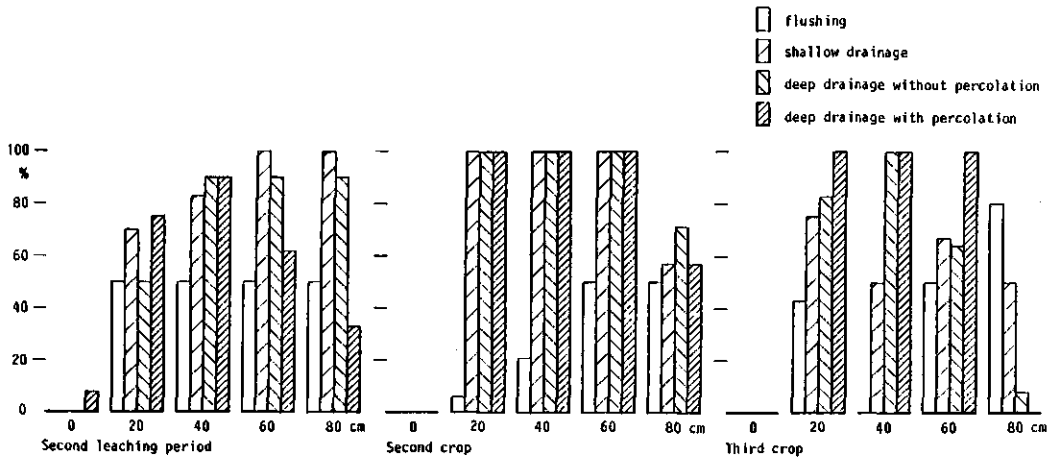


Fig. 2.27 Frequency of occurrence of Fe²⁺ concentrations of the soil solution above 500 ppm at different depths in Sinacaban acid sulphate soil during the second leaching period and the second and third crops (treatments: 2.5 t/ha of lime, all water management practices).

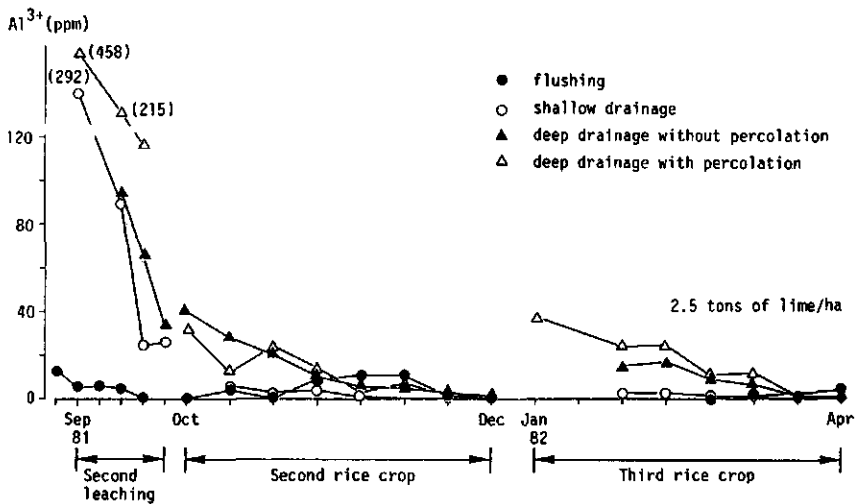


Fig. 2.28 The changes of aluminium concentrations in the soil solutions at 20 cm depth of Sinacaban acid sulphate soil during the second leaching period and the second and third crops (treatments: 2.5 t/ha of lime, all water management practices).

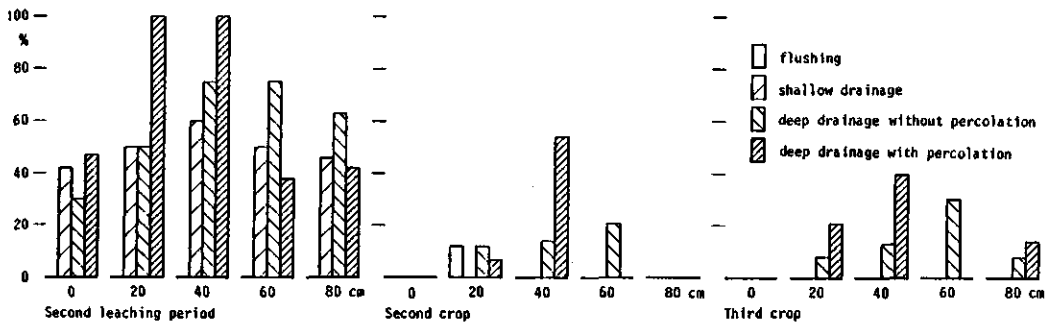


Fig. 2.29 Frequency of occurrence of Al³⁺ concentrations in the soil solution above 40 ppm at different depths in Sinacaban acid sulphate soil during the second leaching period and the second and third crops (treatments: 2.5 t/ha of lime, all water management practices).

treatments during the second crop (Fig. 2.27). With proceeding flooding a lower frequency of occurrence of iron above 500 ppm was observed during the third crop.

-Al³⁺

Aluminium developed during the dry period was removed by imposing drainage treatments. The aluminium concentration in the soil solution of both the shallow and the deep drainage treatments dropped to about 30 ppm at the end of the leaching period and gradually decreased during the second and third crops (Fig. 2.28). Similar to no lime application, the frequency of occurrence of aluminium above 40 ppm was nil at 40, 60, 80 cm depths for both the shallow drainage and the flushing treatments (Fig. 2.29).

* Effects of mulch during dry season on the chemical properties of Sinacaban soil

-pH

The changes of the pH values in the soil solution at 20 cm depth below the soil surface of the mulch and the flushing treatments during the leaching period and the second and third crops is presented in Fig. 2.30. pH values were higher in mulch treatments than those without. Mulch reduces the soil evaporation, thus decreases the oxidation rate, resulting in a lesser development of acidity. During the second and third crops, the pH values were well above 4. The pH values gradually increased with time in the shallow drainage treatment without mulch for both cropping seasons. A lower frequency of occurrence of pH values in the soil solution below 3.5 at lower depths was observed in the mulch treatment (Fig. 2.31).

-EC

The electrical conductivity dropped to about 4 mS/cm after the flushing and the shallow drainage were imposed (Fig. 2.32). The highest EC values were found in the shallow drainage treatments without mulch during the second crop. This may be attributed to the upward movement of salts from lower depths by diffusion and capillary transport with mulch sup-

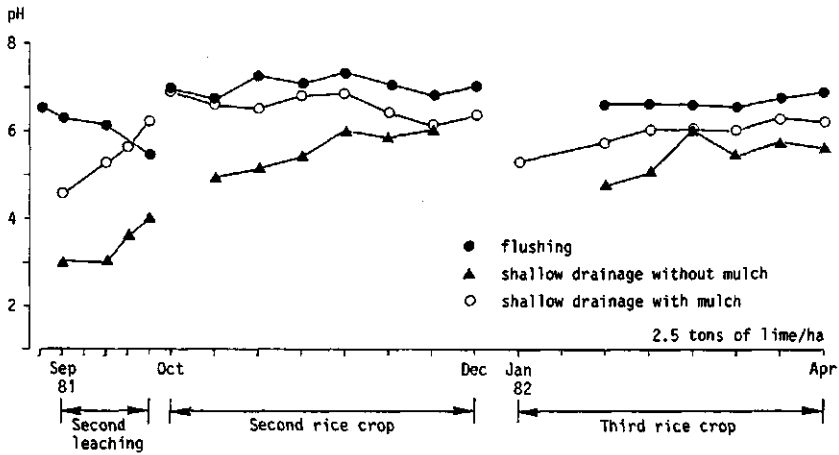


Fig. 2.30 The changes of the pH values in the soil solution at 20 cm depth of Sinacaban acid sulphate soil during the second leaching period and the second and third crops (treatments: 2.5 t/ha of lime, surface flushing and mulch practices).

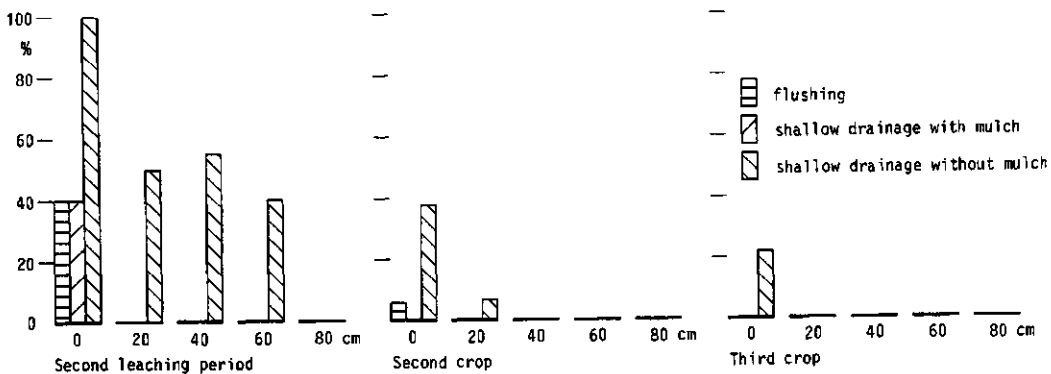


Fig. 2.31 Frequency of occurrence of the pH values in the soil solution below 3.5 at different depths in Sinacaban acid sulphate soil during the leaching period and the second and third crops (treatments: 2.5 t/ha of lime, surface flushing and mulch practices).

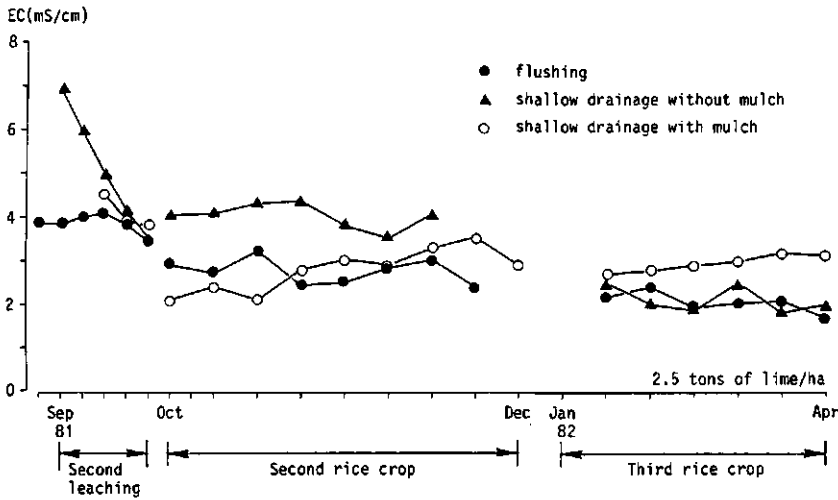


Fig. 2.32 The changes of EC values in the soil solution at 20 cm depth of Sinacaban acid sulphate soil during the second leaching period and the second and third crops (treatments: 2.5 t/ha of lime, surface flushing and mulch practices).

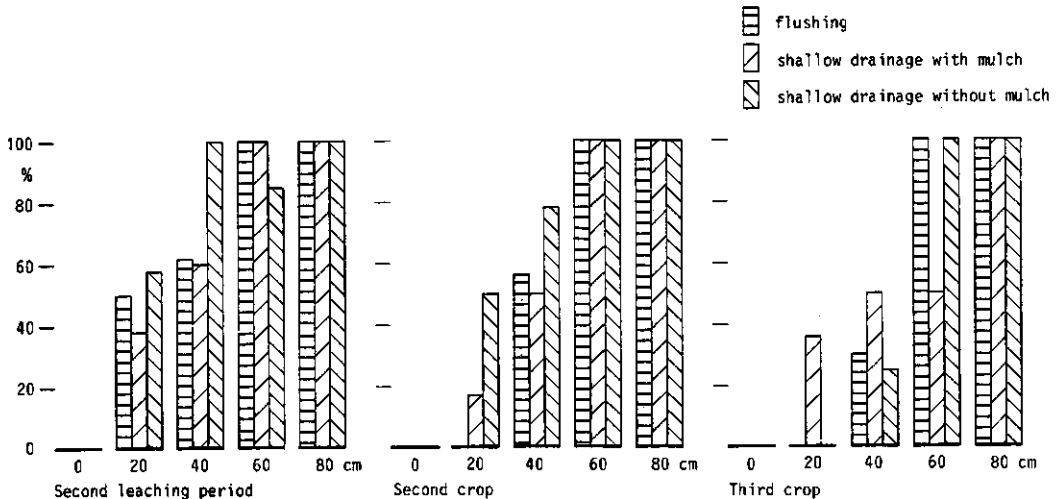


Fig. 2.33 Frequency of occurrence of EC values in the soil solution above 4.0 at different depths in Sinacaban acid sulphate soil during the second leaching period and the second and third crops (treatments: 2.5 t/ha of lime, surface flushing and mulch practices).

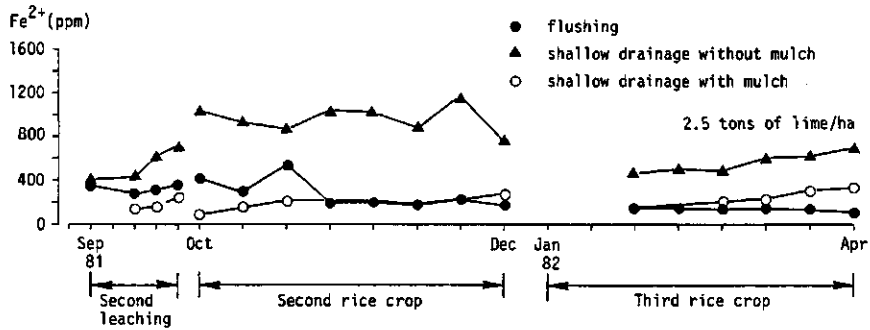


Fig. 2.34 The changes of iron concentrations in the soil solution at 20 cm depth of Sinacaban acid sulphate soil during the second leaching period and the second and third crops (treatments: 2.5 t/ha of lime, surface flushing and mulch practices).

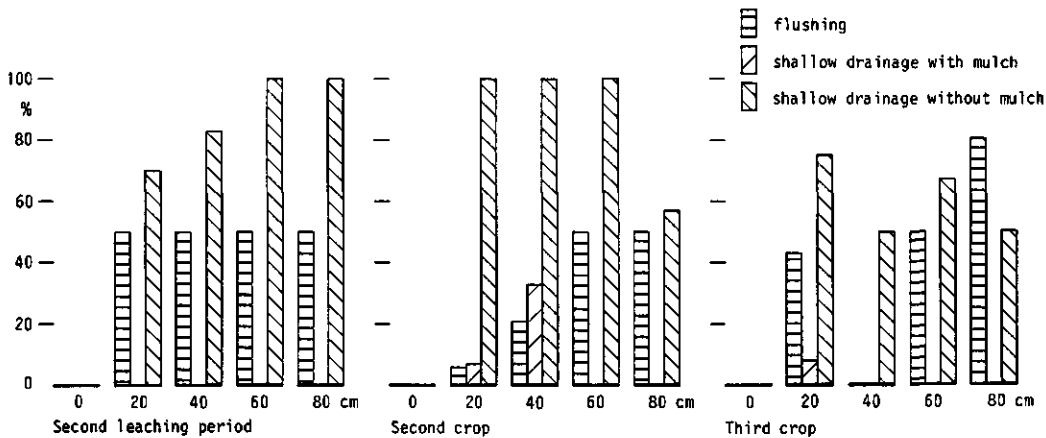


Fig. 2.35 Frequency of occurrence of the Fe²⁺ concentrations in the soil solution above 500 ppm at different depths in Sinacaban acid sulphate soil during the second leaching period and the second and third crops (treatments: 2.5 t/ha of lime, surface flushing and mulch practices).

pressing the latter. The frequency of occurrence of EC values lower than 4 mS/cm at 40 cm depth in the shallow drainage treatments with mulch was 50 percent as compared to 78 percent of those without mulch (Fig. 2.33).

-Fe²⁺

Mulch markedly influenced the iron concentration in the soil solution at 20 cm depth below the soil surface (Fig. 2.34). The average iron concentrations of the mulch treatments during the second crop was about 200 ppm as compared to 1000 ppm of the no mulch treatments. Lower iron concentration in mulch treatments was attributed to smaller amounts of oxidation products. This coincides with the lower frequency of occurrence of iron in the soil solution above 500 ppm at different depths in the shallow drainage treatment with mulch (Fig. 2.35). There was only a slight variation of iron concentrations with time in both the flushing and the shallow drainage treatments with mulch (Fig. 2.34).

-Al³⁺

The shallow drainage treatment without mulch produced large amount of aluminium during the dry season (Fig. 2.36). The aluminium together with other ions were removed from the soil profile when the drainage treatments were imposed.

Drainage without mulch brought down aluminium concentration to about 30 ppm at the end of the leaching period (Fig. 2.36). Shallow drainage with mulch and the flushing caused similar aluminium concentration patterns during the leaching period, and the second and third crops (Fig. 2.36).

Because the soil at lower depths (> 40 cm) was kept saturated with water during the experiment, no oxidation took place, and the frequency of occurrence of Al above 40 ppm in both drainage treatments was nil (Fig. 2.37).

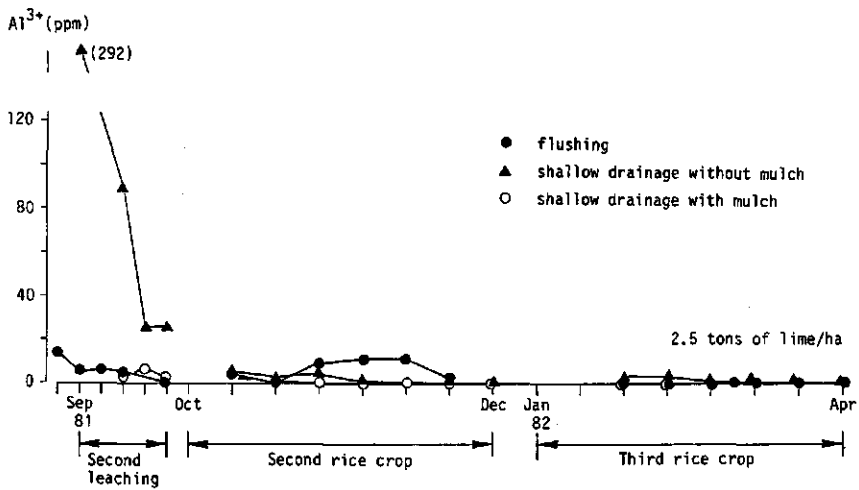


Fig. 2.36 The changes of the aluminium concentrations in the soil solution at 20 cm depth of Sinacaban acid sulphate soil during the second leaching period and the second and third crops (treatments: 2.5 t/ha of lime, surface flushing and mulch practices).

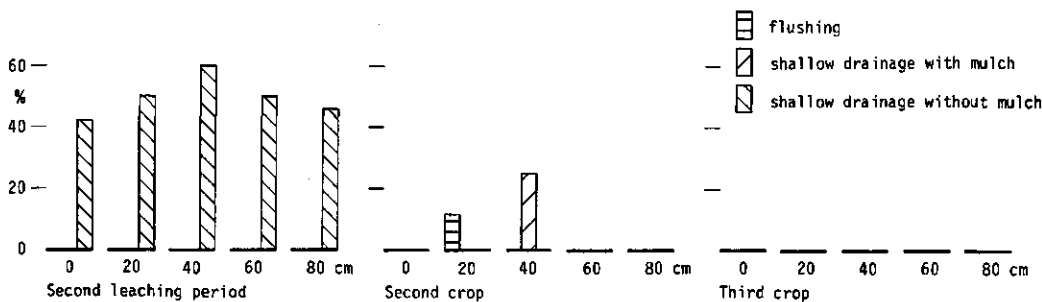


Fig. 2.37 Frequency of occurrence of Al³⁺ concentrations in the soil solution above 40 ppm at different depths in Sinacaban acid sulphate soil during the second leaching period and the second and third crops (treatments: 2.5 t/ha of lime, surface flushing and mulch practices).

General discussion on chemical properties of Sinacaban acid sulphate soil

Although there are some variabilities of the chemical properties within the same treatment, the following points related to the influence of agronomic and water management practices on the chemical properties of the soil solutions can be summarized:

- Lime has markedly decreased the iron and aluminium concentrations in the soil solution at 20 cm depth at deep drainage treatments during the second and third crops. It had no detectable influence on pH.
- With deep drainage of this soil, pH drops to a very low value and produces a large amounts of Fe^{2+} and Al^{3+} as compared to the shallow drainage. The reduction processes during the following cropping seasons were retarded in the deep drainage treatments.
- Mulching with 5 cm of rice straw minimizes the water loss by evaporation, and reduces the oxidation rate. This results in a lesser development of acidity and less Fe^{2+} and Al^{3+} products.
- When the soil is continuously flooded with water, no pyrite is oxidized resulting in low acidity and low Fe^{2+} and Al^{3+} .

2.3.5 Effects of water management and agronomic packages on the grain yield of rice in two acid sulphate soils

The grain yields of the three rice crops in both soils are presented in Tables 2.10, 2.11 and 2.12. Because statistical tests of significance cannot be adequately based on two replicates only, values of each replicate and means are presented to indicate the results of this experiment. Grain yield data of different treatments are given separately for various treatments, e.g. drainage, liming and agronomic packages. Obviously, grain yields differed greatly among the two soils and three cropping seasons.

Table 2.10 Grain yield of rice in two acid sulphate soils, wet season, 1980 (first crop) for each of the treatments applied.

Treatment	Grain yield (g/drum)					
	Aparri soil			Sinacaban soil		
	Replicate		Average ¹⁾	Replicate		Average
	1	2		1	2	
1	148.5	164.4	156.4	155.7	160.5	158.1
2	145.3	161.9	153.6	126.3	132.3	129.3
3	110.8	126.8	118.8	136.5	152.5	144.5
4	162.4	143.5	152.9	105.6	129.7	117.6
5	128.2	151.1	139.7	130.7	172.6	151.6
6	131.0	202.0	166.5	144.3	164.9	154.6
7	134.1	163.0	148.5	155.1	159.8	157.4
8	133.7	138.8	136.2	0.0	64.0	32.0
9	138.5	150.4	144.5	138.5	159.3	148.9
10	155.2		155.2 ²⁾	58.5		58.5 ²⁾
11	135.5		135.5 ²⁾	134.1		134.1 ²⁾

1) Average of two replicates

2) Only one yield replicate available

2.3.5.1 Aparri acid sulphate soil

The grain yield varied with the cropping season (Tables 2.10, 2.11 and 2.12). As expected, the grain yields of different treatments in the first cropping season showed little variation (Table 2.10), because the soil was continuously kept at water saturation and no acidification took place. Contrary to expectation, however, there was also no marked effect of drainage, lime application or agronomic practice on grain yield in the second and the third crop (Table 2.11 and 2.12).

Before transplanting the second and third crops, the pH value of the

Table 2.11 Grain yield of rice in two acid sulphate soils, dry season, 1981 (second crop) for each of the treatments applied.

Treatment	Grain yield (g/drum)					
	Aparri soil			Sinacaban soil		
	Replicate		Average ¹⁾	Replicate		Average
	1	2		1	2	
1	91.9	105.8	98.9	0.0	12.2	6.1
2	105.7	24.5	115.1	0.0	0.0	0.0
3	136.0	144.0	140.0	0.0	0.0	0.0
4	87.6	132.4	110.0	0.0	0.0	0.0
5	97.9	109.0	103.4	0.0	0.0	0.0
6	106.4	140.8	123.6	0.0	102.8	51.4
7	92.8	127.2	110.0	34.7	95.3	65.0
8	88.2	146.4	117.3	68.7	109.0	88.9
9	118.4	118.8	118.6	93.4	118.3	105.9
10	83.5		83.5 ²⁾	90.0		90.0 ²⁾
11	141.5		141.5 ²⁾	0.8		0.8 ²⁾

1) Average of two replicates

2) Only one yield replicate available

soil solution in the surface soil was well above 5.0, regardless of treatment. The relatively high pH value (Table 2.6) and the low values of dissolved iron in the surface soil layer (less than 100 ppm) indicated that Aparri soil was not influenced by pyrite oxidation during the dry period. This was confirmed by the pH values of the pyritic substratum which also stayed rather constant through drainage periods.

Apparently, soil acidity in this soil is not severe enough to hamper the growth of rice. Indeed, draining the soil did not affect the grain yield. This confirms the earlier conclusion that Aparri is not a problem soil.

Table 2.12 Grain yield of rice in two acid sulphate soils, dry season, 1982 (third crop) for each of the treatments applied.

Treatment	Grain yield (g/drum)					
	Aparri soil			Sinacaban soil		
	Replicate		Average ¹⁾	Replicate		Average
	1	2		1	2	
1	289.4	320.1	304.8	0.0	196.0	98.0
2	316.6	342.5	329.5	0.0	0.0	0.0
3	298.6	340.7	319.6	1.2	125.0	63.1
4	289.9	322.9	306.4	198.8	338.3	268.6
5	252.1	334.7	293.4	0.0	92.2	46.1
6	280.9	289.2	285.0	0.0	346.4	173.2
7	271.4	348.5	309.9	202.8	319.9	261.4
8	266.4	295.08	281.1	275.6	293.2	284.4
9	287.8	343.0	315.4	322.2	359.7	341.0
10	270.7		270.7 ²⁾	234.4		234.4 ²⁾
11	283.9		283.9 ²⁾	292.5		292.5 ²⁾

1) Average of two replicates

2) Only one yield replicate available

2.3.5.2 Sinacaban acid sulphate soil

* First cropping season

After the installation of the various instruments in the drums, the various treatments were applied and IR 36 was transplanted. During this season the soils did not undergo a drying treatment, so the oxidation was minimal (Table 2.7). As a result the grain yields (Table 2.10) were hardly affected by treatments, except in one lysimeter (8₁) which had leaked during transportation, causing pyrite oxidation and producing a large amount of acidity which was not leached out sufficiently. Plants

in this lysimeter therefore suffered from severe stresses: low pH, high Al and Fe concentrations and died after some weeks.

* Second and third cropping seasons

In the following sections, the effects of drainage, lime and agronomic practices will be presented and discussed.

. Effects of water management treatments at zero lime

The influence of different water managements at zero lime on the grain yield of rice is presented in Fig. 2.38. The grain yield in drums with the deep drainage treatment was poorest in both the second and the third season (Fig. 2.38). The highest yields were obtained with the flushing treatment, the next highest with shallow drainage. Grain yields of the third crop were considerably higher than those of the second crop. The differences can be ascribed in part to more favourable soil conditions during the third crop: toxic elements were partly removed by leaching in the previous drainage period and by reduction processes during the second crop. The depression of the grain yields in the deep drainage treatment was associated with high acidity, high Fe^{2+} concentration and low pH values in the soil solution (Fig. 2.14 and 2.18).

. Influence of flushing

The grain yields in the flushing treatments were superior to those in the deep and the shallow drainage treatments, both in unlimed and in limed soils (Fig. 2.38 and 2.39). The yields of the third crop were about 300 percent higher for the flushing, the shallow and the deep drainage treatments, respectively, compared to the second crop.

. Influence of percolation on the grain yield of the deep drainage treatments

Contrary to expectation, the grain yields in the deep drainage treatment were lower with percolation as compared to without at 2.5 tons of lime/ha (Fig. 39). This can be explained by incomplete removal of acidity and by soil variability.

With deeper drainage, the contact between soil and air increases, and

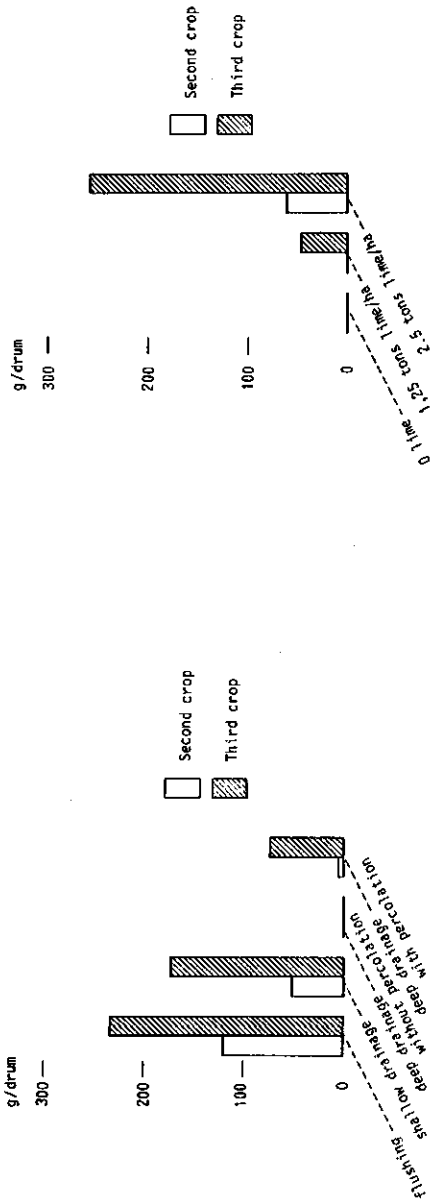


Fig. 2.38 The grain yield of rice during the second and third crops in Sinacaban acid sulphate soil (treatments: 0 t/ha of lime, all water management practices).

Fig. 2.40 The grain yield of rice during the second and third crops in Sinacaban acid sulphate soil (treatments: deep drainage, three lime levels).

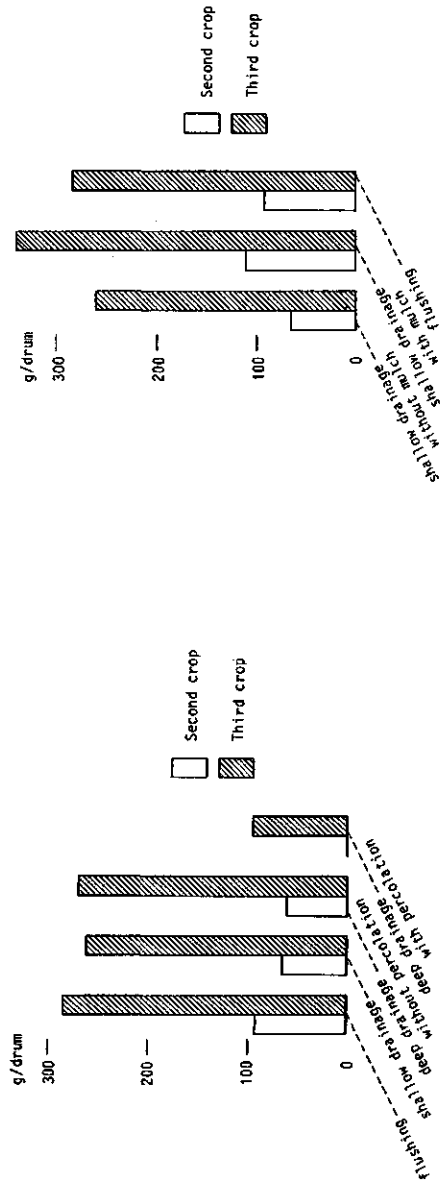


Fig. 2.39 The grain yield of rice during the second and third crops in Sinacaban acid sulphate soil (treatments: 2.5 t/ha of lime, all water management practices).

Fig. 2.41 The grain yield of rice during the second and third crops in Sinacaban acid sulphate soil (treatments: 2.5 t/ha of lime, surface flushing and mulch practices).

oxidation and acidification intensify. Because the acidity developed during oxidation was not sufficiently removed by leaching, or was neutralized by liming, oxidation due to deep drainage had detrimental effects to rice plant. Upward diffusion of Fe^{2+} to the surface water followed by oxidation of Fe^{2+} to ferric hydroxide, produced appreciable amounts of acidity in the surface water. The acidity gradient between the surface water and the soil solution of the upper soil layers may cause a downward movement of acidity to the surficial roots of young rice plants. This high acidity hampered the root development and as a result the growth of rice was retarded.

. Influence of lime levels in the deep drainage treatments

The rice of the second crop failed completely, both at the application of 0 and of 1.25 tons of lime/ha, due to the excess acidity (Fig. 2.40). Only after increasing the amount of lime up to 2.5 tons/ha, the rice produced some yield, due to the decreased acidity. In the third crop, the soil toxicity had apparently been decreased so much by leaching and chemical reduction that also at a low dose of lime, the rice yielded about 40 g/ drum. The acidity remained very high in the treatment without lime (Fig. 2.6).

. Influence of mulch on the grain yields of rice at an application of 2.5 t/ha of lime

The influence of mulch on the grain yield of the second and third season was clear (Fig. 2.41). Mulching increased grain yield of the second and third crops with 67 and 30 percent, respectively. Mulch helped to conserve moisture in the profile (Table 2.5), to minimize pyrite oxidation and to produce less acidity. The differences in grain yields of the two cropping seasons may be due to the differences in chemical properties of the soil and to climatological factors. The results of this experiment indicate that mulching is a promising treatment for this soil.

. Occurrence frequency of successful crops under different water management practices

The results of the experiment with different water management practices of the Sinacaban soil on the grain yield may be illustrated by showing the frequency of successful crops. A "successful crop" is defined in our case as a crop with a yield of at least 1 ton/ha or 60 g/lysimeter. For example, if three out of the four replicates gave more than 60 g per drum, the frequency of successful crops was indicated as 75%. Irrespective of the lime levels, the crops were 100% successful after flushing (Fig. 2.42). This success is not dependent on lime application. At zero lime level, the crops were found to be 50% and 0% successful after the shallow and the deep drainage treatments, respectively. Increasing lime levels from 1.25 to 2.5 tons/ha increased the frequency of successful crops for both levels after the shallow and the deep drainage. The deep drainage treatment was generally the least successful revealing the hazardous nature of this treatment. The acidity, developed in the deep drainage treatment could only be removed with large amounts of water for leaching.

The data presented in Figure 2.42 are indicative rather than conclusive; the danger of deep drainage should be taken into account in

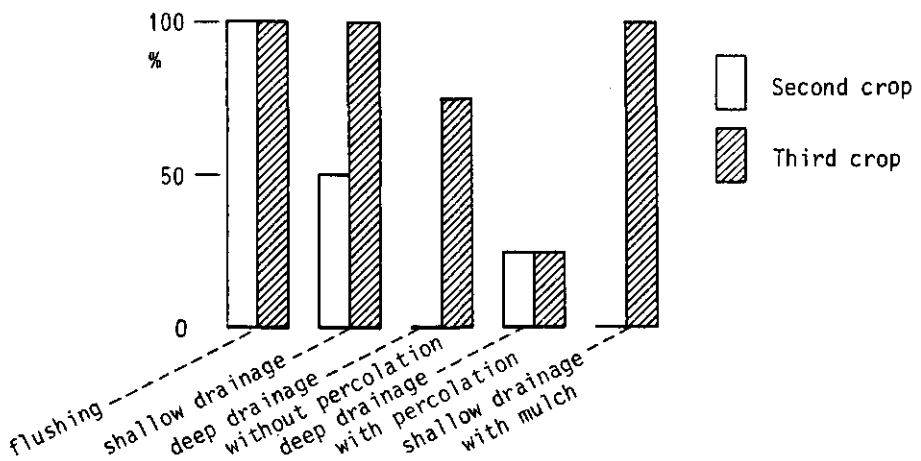


Fig. 2.42 Occurrence frequency of successful crops under different water management practices for the second and third crops in Sinacaban acid sulphate soil.

planning any reclamation project, where water or time is a limiting resource. In the case of potential acid sulphate soil, prevention is better than curative treatment.

. Grain yield in relation to chemical changes of stagnant surface water and of the soil solution of the surface soil

Water management and agronomic practices influence the chemical status of the acid or potential acid sulphate soils. The chemical status of the soil in turn influences the performance of rice. So far, no model is available, which relates grain yield and condition of the soil solution during the crop growth period. A pH value as low as 3.5 did not, by itself, have a harmful effect to rice (Thawornwong and van Diest, 1974; Le ngoc Sen, 1982b). Iron concentrations in the soil solution higher than 500 ppm are toxic (Mai thi My Nhung and Ponnampereuma, 1966) and aluminium of 20-40 ppm caused aluminium toxicity. Based on these known threshold values, a combined effect of these factors was used to correlate with the grain yields. A score of 1 was set separately for pH between 3 and 3.5, dissolved iron greater than 500 ppm and for aluminium concentrations greater than 30 ppm for each observation during the growth period. Otherwise a zero-score was assigned. The total number of scores was then divided by the number of observations. The average of the three ratios, expressed as percentage, is called the average mineral stress index (AMSI). If pH of the surface water was less than 3, the AMSI was set to 100%. This index is then used to correlate with the logarithm of the grain yields. Data from Mai thi My Nhung and Ponnampereuma (1966) were used to correlate the logarithm of grain yields and AMSI calculated by method mentioned above. This graph showed a linear correlation (Fig. 2.43).

The correlation between the logarithmic grain yields and average mineral stress index for the second and third crops in Sinacaban acid sulphate soil are presented in Fig. 2.44. In the second crop two distinct regions could be distinguished: at AMSI less than 40% the grain yields ranged from 20 to 90 g per drum, and if AMSI equals 100%, the grain yields were always zero. There was no correlation between grain yields and AMSI at lower AMSI values, which may be due to other factors such as salinity or microclimate.

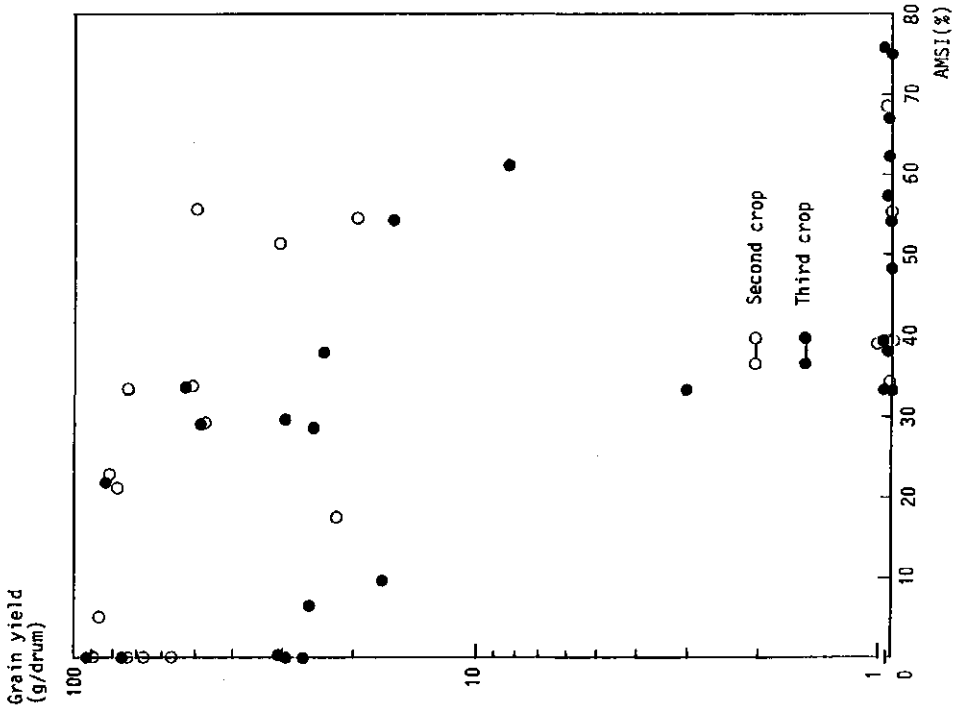


Fig. 2.44 The relation between the logarithmic grain yield and AMSI.

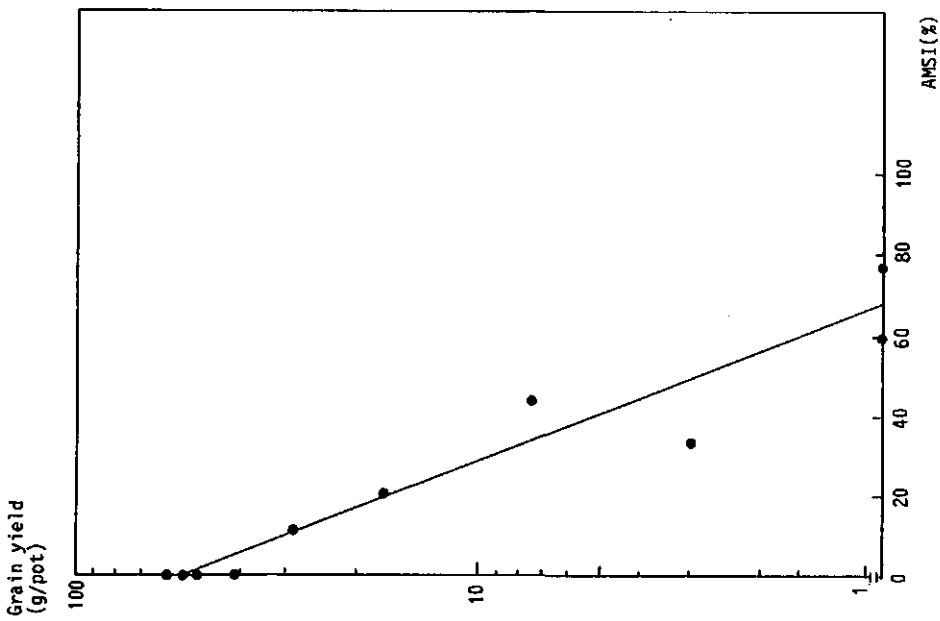


Fig. 2.43 The relation between the logarithmic grain yield and AMSI based on data of Mai thi My Nhung and Pounnamperuma, 1966.

2.4 Summary and conclusions

The influence of different agronomic and water management practices on the growth of rice and on the chemical changes of Aparri and Sinacaban acid sulphate soils were studied in forty undisturbed soil cores (60 cm diameter, 90 cm deep) subjected to different water management practices, liming rates and mulch application for two leaching periods and three rice crops. IR36 rice variety was transplanted. Surface water and soil solutions at 20, 40, 60 and 80 cm depths were collected for pH, EC, Fe^{2+} and Al^{3+} determination.

There was a great difference in chemical properties and grain yield of the two soils.

In Aparri soil, there was no marked effect of drainage, liming and agronomic practices on the chemical properties of the soil solution during the two leaching periods and during the three rice crops. These associated with the well developed and mature surface soil and the minimal pyrite oxidation in the subsoil. The grain yields of the three crops were high and were not influenced by different treatments.

In Sinacaban soil, however, the effects of drainage, liming and agronomic practices on the chemical properties of the soil solutions were very pronounced. Imposing deep drainage to the soil created favourable conditions for pyrite oxidation, which resulted in high acidity production and higher Fe^{2+} and Al^{3+} . The frequency of occurrence of pH values less than 3.5 was 100 percent in the subsoil layers below 40 cm. Shallow drainage did not cause severe oxidation in the subsoil layers and produced less acids and lower Fe^{2+} , Al^{3+} concentrations. Shallow drainage in combination with a mulch application (5 cm of rice straw) minimized water loss from the soil, and hindered oxygen movement to the subsoil. This resulted in less acid development and lower Fe^{2+} , Al^{3+} concentrations. When the soil was continuously submerged, no pyrite oxidation took place, nor any production of Fe^{2+} and Al^{3+} ions. The reduction process followed the same trend as in other experiments from surface materials of acid sulphate soils reported by Mai thi My Nhung and Ponnampertuma (1966). Even with prolonged submergence, reduction was very slow in the subsoil layers. The acidity and the Fe^{2+} concentration

remained very high for a long period (9 months). The aluminium concentration decreased with increasing pH-values of the soil.

In Sinacaban soil, during the first cropping season, grain yields were hardly affected by treatments, because the soils did not undergo a drying period. During the second and third cropping seasons, the influence of different treatments on grain yields was very pronounced. The deep drainage treatment gave the poorest yields of both the second and third crops. Highest yields were obtained with the surface flushing treatment, the next highest yields with the shallow drainage. Irrespective of lime levels, the grain yield in the deep drainage treatments was lower with percolation than without. Mulching increased the grain yields of the second and third crops by 67 and 30 percent, respectively. In the deep drainage treatment, only high amounts of lime, 2.5 tons/ha, produced a yield exceeding the equivalent of about 1 t/ha. The frequency of occurrence of "successful crops" under different practices revealed the superiority of the flushing treatment. The concept of the average mineral stress index (AMSI) was introduced to correlate grain yield and toxic elements in acid sulphate soils (pH, Fe^{2+} and Al^{3+}), but the correlation was less pronounced than that obtained from results found by Mai thi My Nhung and Ponnampetuma (1966).

The provisional management measures to increase rice production in acid sulphate soils areas are the following: Well developed, mature acid sulphate soils with a pyritic layer deeper than 40 cm (sulphic Tropaequet of the Aparri type), are hardly subject to acidification, even when the ground water table is lowered to 80 cm below soil surface. Therefore attention should be focused on the source of water for washing out the excess salt (if the soil is saline) and on the fertilization practices.

The potential acid sulphate soils of Sinacaban type will produce a large amount of acids upon drainage. Reclamation measures are therefore largely dependent on the water availability. In areas with sufficient water, the soil should be kept continuously flooded and in areas, where water is scarce during some parts of the year, shallow drainage in combination with mulch is most likely to reduce the problems.

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Appendix 2.1

Acid sulphate soil near Aparri, Philippines

USDA Soil Taxonomy: Sulphic Tropaquept. Profile Aparri, examined and sampled 1 November 1979 by Le ngoc Sen and Robert Brinkman.

The site

Location near Aparri, Cagayan, Philippines. About 3 km SE of Aparri, about 0.5 km E of small tidal creek. Map reference Philippines 1:50.000 scale, sheet 3375 III, Aparri, 18° 21' N, 121° 40' E.

About 1 m above mean sea level.

Landform and slope: young Holocene coastal plain, level.

Vegetation/land use: bunded wetland fields, grass fallow. Until a year ago: open short grass and sedge swamp.

Climate: tropical monsoon climate; occasional typhoons; occasional salt-water flooding.

General information on the soil

Parent material: Holocene marine alluvium

Drainage poor. Seasonally flooded to moderate depth. Moisture conditions in the soil: upper few mm dry, moist to wet below. Ground water at about 70 cm depth.

No surface stones or rock outcrops. No erosion except very locally along tidal channels. Occasional salt-water flooding.

Human influence: field bunds and ploughing to 8 cm, started about 1 year ago.

Brief description of the profile

Deep, poorly drained, very dark grey silty clay with a greyish brown, distinctly mottled subsoil and a wet, black to very dark grey, plastic and sticky substratum. Structure is weak prismatic and blocky; the soil is moderately porous throughout.

Profile description

Ap, 0-8 cm. Very dark grey (10YR3/1) moist silty clay; few fine distinct strong brown mottles; massive; dry hard, moist to wet plastic, nonsticky; common fine tubes; many fine living and dead roots; clear smooth boundary.

A1, 8-25/30 cm. Very dark grey (10YR3/1) moist silty clay; common fine distinct brown (7.5YR4/4) mottles along root channels, many medium distinct brown along prism faces in upper 5 cm, few in lower part; moderate very coarse prismatic; moist to wet plastic, nonsticky; thin continuous cutans on prism faces; common fine tubes and many fine roots, both mainly vertical; clear wavy boundary.

Bg, 25/30-40/46 cm. Greyish brown (10YR5/2) moist silty clay; many medium distinct light yellowish brown, brownish yellow and brown/dark brown mottles; weak coarse prismatic and moderate coarse and medium angular blocky; moist to wet plastic, nonsticky; thin patchy cutans on all faces; common fine mainly vertical tubes; common fine living and dead roots; clear wavy boundary.

Cg1, 40/46-60 cm. Black (10YR2/1) moist silty clay; only along ped faces, common fine distinct dark reddish brown mottles with common fine distinct brownish yellow mottles in upper part; moderate coarse prismatic and weak medium angular blocky; wet plastic, nonsticky; common fine vertical tubes and roots; gradual smooth boundary.

Cg2, 60-90 cm. Very dark grey (10YR3/1) moist silty clay; common fine faint dark brown mottles along root channels and few medium faint dark reddish brown mottles along coarser pores; weak very coarse prismatic and very weak medium angular blocky; wet plastic and sticky; common fine mainly vertical tubes and roots; diffuse boundary.

CG, 90-110+ cm. Very dark greyish brown (10YR3/2) silty clay; many medium distinct greyish brown mottles with indistinct limits; massive and very weak angular blocky; wet plastic, very sticky; common fine tubes and roots.

Acid sulphate soil in Sinacaban, Philippines

USDA soil taxonomy: Typic Sulfaquent. Profile Sinacaban was examined and sampled on April 19, 1980 by Le ngoc Sen.

The site

The site is located in barrio Tidok, Sinacaban, Misamis occidental, Philippines and is an uncultivated land with mangrove trees. This area will turn into fishponds in the near future. Nearby the site, wetland rice was cultivated and some fishponds were under operation.

Rainfall is ample in this place (>5.000 mm) and evenly distributed throughout the year.

The site is influenced by diurnal tide. The difference between the high and low tides is about 1 m. During the high tide the soil is submerged to about 10-20 cm above the soil surface. During the low tide, ground water is found at about 30 cm below the soil surface.

The topography of the site is flat. Many lobster mounds appears on the soil surface (pH < 3) of this area.

In the newly constructed fishponds nearby, intensive jarositic mottles were found on the dikes.

Profile description (from auger samples)

- A₁: 0-10/15: color 10YR3/2, silty loam, non sticky. The dominant mottles having color 2YR3/6, with the density of 10-20/dm² partly from dead mangrove leaves and from the eroded materials of the adjacent mountains. There are fresh mangrove roots of 0.5-2 mm in diameter and crab holes of 10 mm in diameter. Low organic matter.
- A₂: 10/10-20/25 mm: color 10YR3/2. Less mottles than the upper layer. No crab holes. Soil is relative stickier than the upper layer, low organic matter.
- A₃: 20/15-40: color 10YR4/1. Slightly sticky, high organic matter. Clay loam. Root channels had a size of less than 1 mm in diameter. Mottles color 2YR3/6.
- C₁: 40-70: Very loose material high organic matter, color 10YR3/2.
- C₂: 70-100: The color of soils is 10YR3/2, very high organic matter. Some fresh mangrove roots appear.
- C₃: >100: sandy material, gravel of >1 cm appear and big mangrove roots are found.

THE EVAPORATION AND ACIDIFICATION PROCESS IN AN ACID SULPHATE SOIL

Abstract

Fourteen undisturbed soil columns of 20 cm in diameter and 70 cm length from an acid sulphate soil in Mijdrecht, Netherlands were used to study the acidification process upon drying. Two groundwater levels: 40 cm and 65 cm below the soil surface, 5 different durations of evaporation and 2 agronomic practices were imposed.

Among treatments, averaged total acidity over 14 layers in the soil profile did not show much variation as the cumulative evaporation increased. The depth of the acidity maximum in the soil profile with low groundwater varied with the presence or absence of peat on the surface. Without peat, the total acidity maximum in the soil profile was about 35-40 cm below the surface, with a thin peat layer, they remained about 10 cm deeper.

The presence of peat layer on the surface reduced the rate of acidification, presumably mainly by reducing evaporation rate and perhaps by reducing the input of oxygen in the soil profile.

The average pH value over 14 layers along the soil profile was lowered as the depth of groundwater increased from 40 to 65 cm. In treatments with a low groundwater table, the average pH decreased sharply with increasing evaporation: to about 3.5 after 140 mm of evaporation. The decrease was less drastic where groundwater remained high. Mulching or plowing at the start of a dry season to reduce the flux of solutes by capillary movement and maintaining the water table as high as possible

to reduce oxidation may be good management practices in acid sulphate soils.

4.1 Introduction

The formation of acid sulphate soils results from the presence of sulfides, the introduction of aerobic conditions, and the lack of bases, usually calcium carbonate, to neutralize the acidity. Soils may become aerobic when they are drained for agriculture but also when there are seasonal changes in soil drainage, e.g. by a lowering of the groundwater table. Evaporation from bare soils may have the same effect owing to the loss of soil water. Evaporation may also cause accumulation of toxic salts in surface horizons because of upward capillary movement. Low pH, high acidity and accumulation of toxins can degrade the productivity of the soils. Results of field experiments about the effects of changes in groundwater level on the acidity of acid sulphate soils and on crop yields were reported by Beye (1973), Kanapathy (1973) and Yin and Chin (1982), but basic information about the effect of evaporation in the dry season is lacking. Field observations in Vietnam indicate that plowing in the dry season followed by leaching of salts accumulated just below the surface soil may depress the toxicity to crops in acid sulphate soils (Vo tong Xuan, personal communication). The objective of this study was to determine the effects of groundwater levels and other factors related to the evaporation rate on the acidification process of an acid sulphate soil.

4.2 Materials and methods

An acid sulphate soil from Mijdrecht Polder in the Netherlands was used for this study.

The soil profile consisted of a thin (10 cm) peat layer, somewhat compacted, over 35 cm jarositic material, with a half ripe pyritic substratum. Before the experiment, the peat layer was removed except where stated.

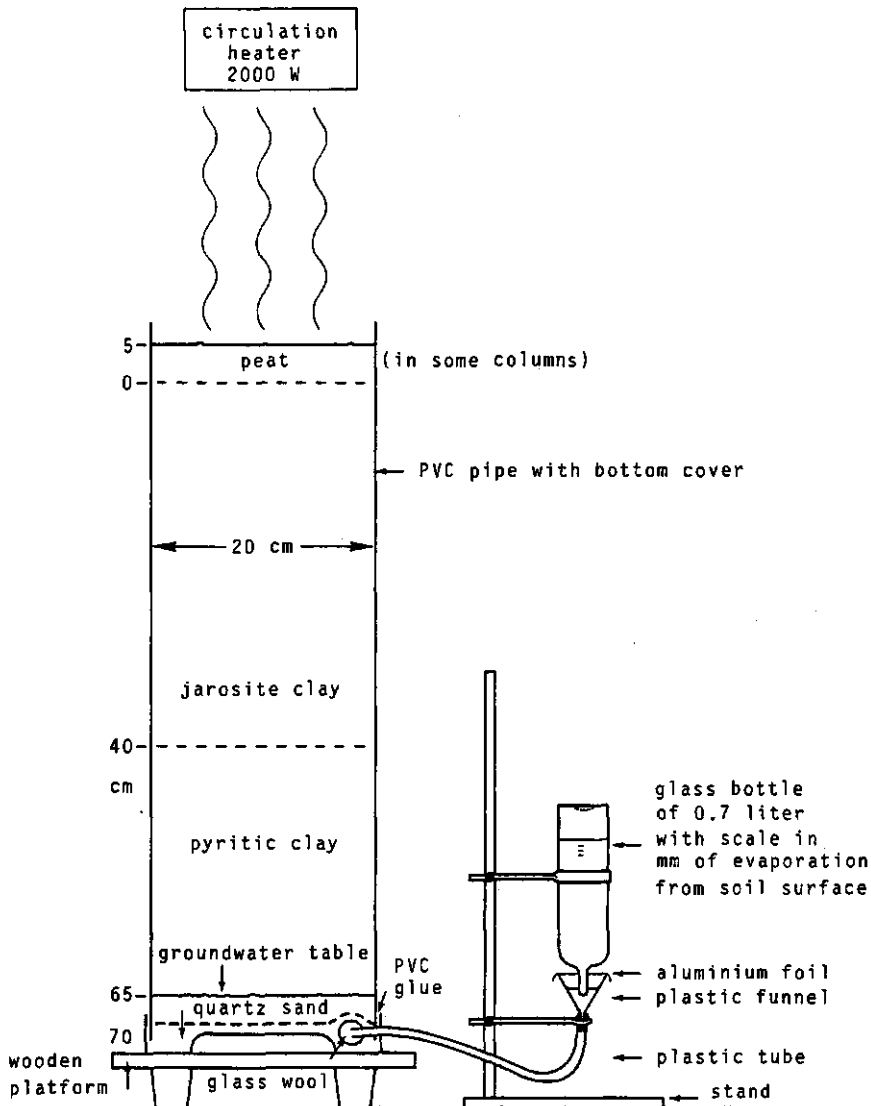


Fig. 3.1 Cross-section of a soil column with low groundwater.

In spite of the artificial drainage in the polder the acid sulphate soil has remained in its poorly drained condition, being protected by a 35 cm thick man-made soil cover. This was removed before sampling. Undisturbed soil columns were collected in 14 PVC pipes with 20 cm inside diameter and 70 cm length (Fig. 3.1). One end of the PVC pipe was sharpened in order to have a good cutting edge. The procedure used in obtaining the columns was similar to that described by Le Ngoc Sen (1982). The columns were excavated in two rows close to each other in an area of 0.5 x 2 m (Fig. 3.2).

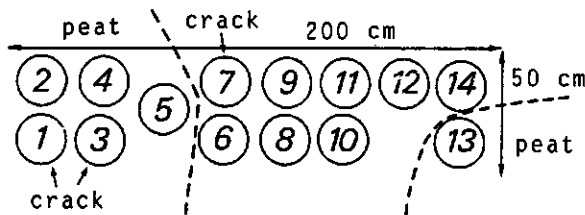


Fig. 3.2 Place of soil columns in the original soil.

The filled PVC pipes were tied with rope, turned 45 degrees and dragged up to the ground surface along the sloping side of the pit. The excess soil material at the bottom was trimmed level with the cutting edge. A PVC cover was placed over the top of the column, which was then inverted and kept wet during transport. In the laboratory, a 1.5 cm layer of soil was removed from the bottom of the pipe, replaced by quartz sand and connected with a plastic tube through a bored hole at the side. The end of the plastic tube inside the pipe was covered with glass wool and the other end connected with a source of water to regulate the groundwater table in the profile (Fig. 3.1). A PVC cover was then sealed to the bottom of the pipe with PVC glue, the column replaced in its original position and the top cover was removed.

Two of the fourteen columns were used as controls and were sampled at the beginning of the experiment. The remaining ones were arranged at random (Fig. 3.3).

groundwater table at 40 cm				surface soil disturbed g.w.t. at 65 cm	
14	7	7	14	14	14
(7)	(13)	(5)	(11)	(1)	(9)
(2)	(8)	(4)	(10)	(6)	(14)
10	5	15	15	10	5
groundwater table at 65 cm					

weeks evap.
directly sampled:
(3) (12)
weeks evap.

Fig. 3.3 Arrangement of soil columns in the laboratory.

Two electrical circulation heaters of 2000 watts placed at 0.50 meter above the surface of the columns increased the evaporation rate.

The depths of ground water were maintained at 40 and 65 cm below the soil surface. Different combinations of treatments were imposed (Table 3.1).

The high groundwater level, 40 cm below the surface was chosen to saturate the pyritic horizons, which started at about that depth. The low groundwater level, 65 cm, should allow some oxidation in the upper part of the pyritic horizons.

At the end of a run, the bottom of each pipe was removed and the pipe itself cut into two along the profile by electric saw. The columns were then sectioned into 5 cm segments. In each segment, two samples of 25 ml were taken with the aid of a PVC auger of 5 cm diameter and placed in plastic bottles, then mixed with 100 ml demineralized water, shaken for one hour and centrifuged for 30 minutes at 3000 rpm. In the supernatant liquid EC and pH were determined electrometrically. Total acidity was determined by titration with 0.1 N NaOH to the end point by phenolphthaleine as indicator. Total acidity comprises three kinds of acid: H^+ , Al^{3+} and Fe^{2+} . The former is neutralized directly during titration, Al^{3+} is hydrolyzed to $Al(OH)_3$ releasing $3H^+$; and Fe^{2+} is oxidized in the mechanically stirred solution during titration, producing $Fe(OH)_3$ and $2H^+$. Vertical moisture distribution was determined

Table 3.1 Characteristics of different soil columns.

Column number	Groundwater level (cm)	Duration of evaporation (weeks)	Plowing surface soil	Presence of peat on surface	Presence of jarositic crack
1	65	14	yes	yes	yes
2	65	10	no	yes	no
3 ¹⁾	--	--	no	yes	yes
4	65	15	no	yes	no
5	40	7	no	yes	no
6	65	10	no	no	no
7	40	14	no	no	yes
8	65	5	no	no	no
9	65	14	yes	no	no
10	65	15	no	no	no
11	40	14	no	no	no
12*	--	--	no	no	no
13	40	7	no	yes	no
14	65	5	no	no	no

1) control column

along all profiles except for the control columns 3 and 12. Bulk samples over 10 cm depth increments were freeze-dried for sulphur fractions and other chemical analyses, according to Begheijn (1980). Samples of columns 4 and 10 were collected in 100 ml aluminium rings for bulk density determination. In the extracts of columns 4, 10 and 11, determinations of Ca, Mg, Na, K, Fe, Cl, NO_3^- , SO_4^{2-} and HCO_3^- were made additionally. Except for HCO_3^- , which was determined by carbon analyzer after centrifugation, these determinations were made on solutions stored in the refrigerator for 2 weeks after adding a few drops concentrated HCl.

Some of the water samples from columns 4, 10 and 11 were also analyzed for Ca, Fe, Mg by atomic spectrophotometer; Na and K by atomic emission spectrometer; Al by spectrophotometer with pyrocatechol violet; Fe, Cl, NO_3^- and SO_4^{2-} by ion-chromatography.

Freeze-dried samples of columns 3, 4, 10 and 12 were used to determine CEC, Ca, Mg, Al and total acidity, and freeze-dried samples of columns 2, 3, 8, 12 and 10 for sulfur fractions.

3.3 Results and discussion

3.3.1 Evaporation

The evaporation rate appeared to be influenced by the level of the groundwater table, by disturbance of the surface soil and by the presence of a peaty layer on the surface. The evaporation rate was about

Table 3.2 Evaporation rate, averaged soil moisture, EC, pH, total acidity and basic cations of different soil columns.

Column number	Evaporation rate (mm/day)	Averaged ¹⁾ soil moisture (mass %)	Averaged EC (mS/cm)	Averaged pH	Averaged total acidity (mol/m ³)	Averaged basic cations (mol/m ³)
1	0.82	85	0.93	3.95	1.71	11.5
2	0.66	102	1.02	3.97	2.07	12.8
3	0.00	-- ²⁾	0.79	3.78	1.04	9.2
4	0.73	94	1.11	3.96	2.50	14.0
5	1.47	88	1.03	4.19	2.12	12.9
6	1.37	92	1.16	3.77	3.01	14.4
7	1.69	93	0.97	3.90	1.78	12.0
8	1.28	87	1.28	4.04	3.44	16.2
9	0.99	88	1.60	3.70	11.84	13.8
10	1.19	85	1.89	3.61	16.96	14.0
11	1.61	92	1.11	3.93	4.56	11.9
12	0.00	-- ²⁾	0.82	4.25	1.74	10.0
13	2.14	92	0.97	4.15	1.77	12.2
14	1.54	95	1.06	4.16	2.16	13.3

1) Averaged value of 7 layers in the soil column

2) Not determined

1.5 to 2.1 mm per day with a high groundwater table and about 0.7 to 1.5 mm per day with a low groundwater table (Table 3.2). This amounts to about 30-60 percent of the evaporation from a free water surface measured in the experiment (3 mm/day). The presence of a peaty layer on the surface decreased the evaporation rate by about 50 percent compared with the columns without peat. Disturbance of the upper 10 cm decreased the rate by about 20 percent.

3.3.2 Sulphur fractions

Four columns subjected to different durations of evaporation were selected for sulphur fraction analysis. Total S, pyrite, jarosite and water-soluble S are shown in Fig. 3.4. In general, total S and pyrite of the four columns showed similar trends along the soil profile: both total S and pyrite increased with depth. The difference in total S and pyrite trends between the treated columns and a control (column 3) may be attributed to the strong microvariability of the soil in the field. The lower pyrite content in column 3 is related to oxidation along a deep crack with a concentration of jarosite in this column; the low average jarosite and water-soluble S contents must have been the result of preferential leaching. Because of the variability between columns, even taken adjacent to each other, no quantitative calculation was made about the rate of oxidation and the results were studied by individual columns.

3.3.3 The distribution of pH, total acidity, non-acid cations and soil moisture in different soil columns

The distribution of pH, total acidity, non-acid cations and soil moisture in water extracts of different soil columns is presented in Fig. 3.5.

pH: In general, the pH of the water extract of samples from all columns showed the same trend along the soil profile (Fig. 3.5): a slight decrease in pH during the first 50 mm of evaporation only in the 40 cm

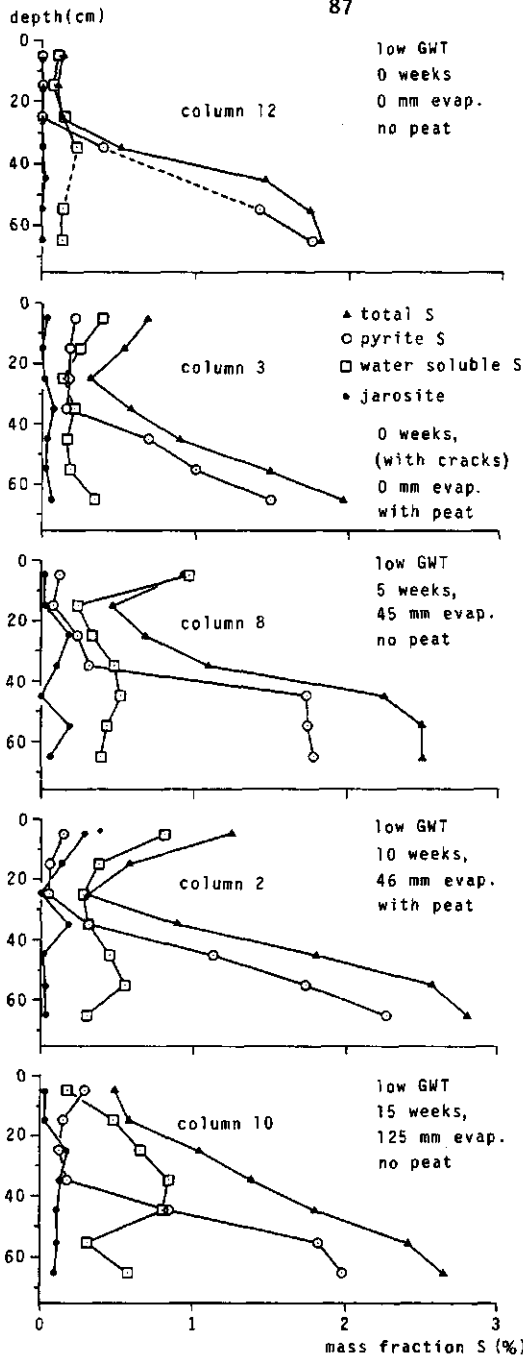


Fig. 3.4 Sulphur fractions of five soil columns with low groundwater table.

surface soil, followed by a drop of half a pH unit throughout the profile as evaporation increased. For columns with a low groundwater level the lowest pH values were observed at the pyrite-jarosite boundary at 35 to 40 cm; with high groundwater, about 5 cm higher (Table 3.3). This difference is attributed to the upward movement of acidity from the oxidation products of pyritic layers.

Table 3.3 Depths of total acidity maximum and pH minimum.

Column number	Groundwater table	Presence of peat	Depths, cm	
			Total acidity maximum	pH minimum
1	low	+	45-50	35-40
2	low	+	40-45	35-40
4	low	+	45-50	40-45
Average	low	+	45-50	35-40
14	low	-	40-45	25-30
6	low	-	40-45	40-45
8	low	-	35-40	35-40
9	low	-	35-40	35-40
10	low	-	30-35	30-35
Average	low	-	35-40	35-40
13	high	+	45-50	25-30
7	high	-	50-55	30-35
5	high	+	40-45	25-30
11	high	-	30-35	35-40
Average	high	+ and -	40-45	30-35
3	control	+	55-60	30-35
12	control	-	45-50	25-30
Average	control	+ and -	50-55	30-35

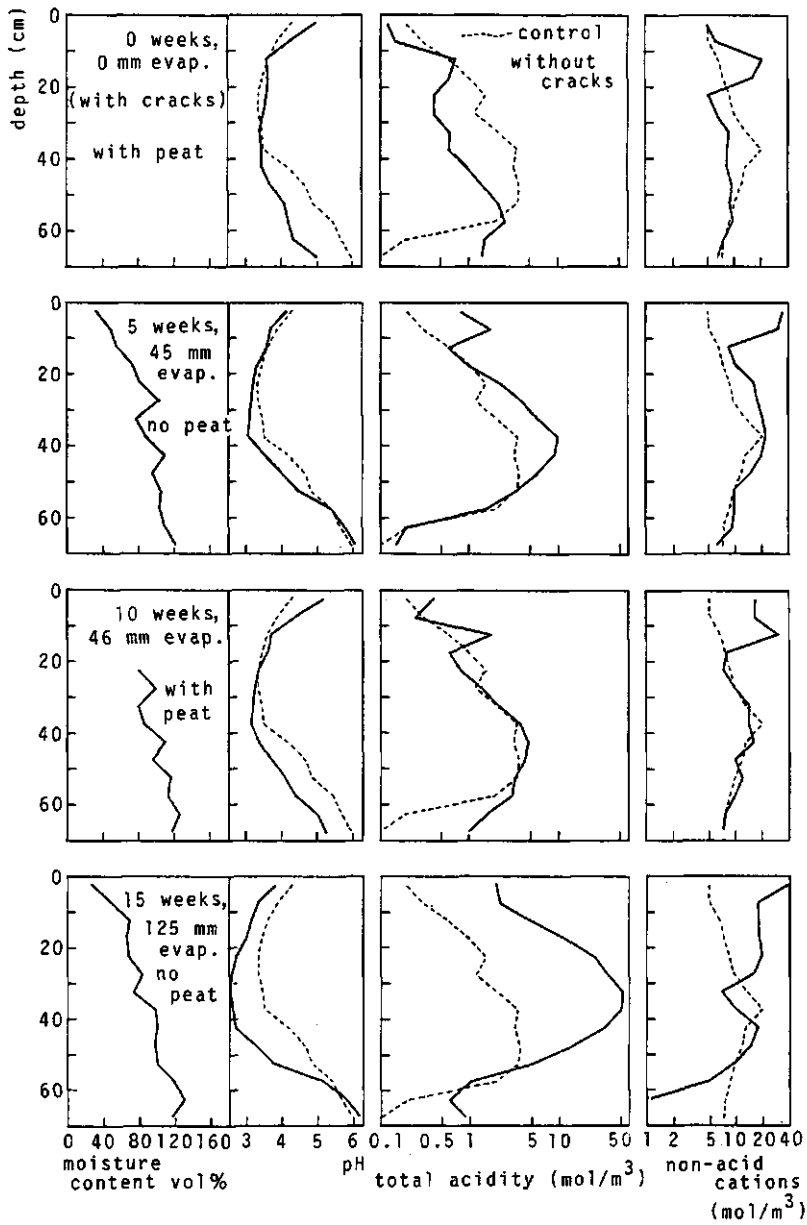


Fig. 3.5 The distribution of soil moisture content and pH, total acidity, basic cations in water extracts of selected soil columns with groundwater at 65 cm depth.

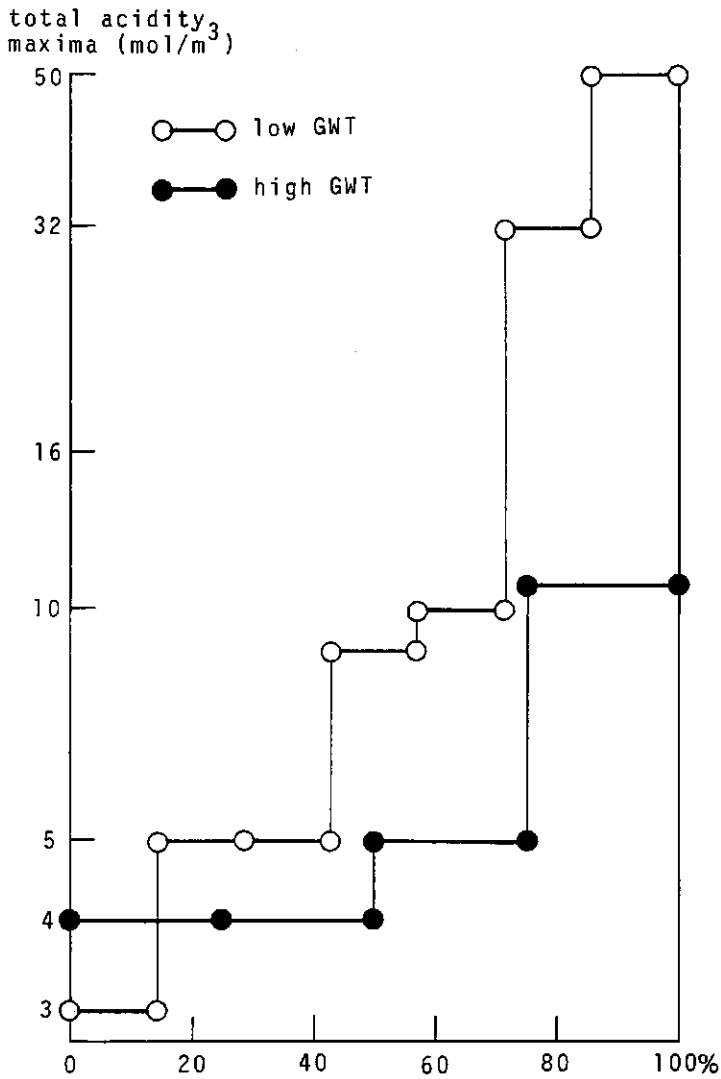


Fig. 3.6 Frequency distribution of total acidity maxima of extracts in the profiles.

3.3.4 Total acidity

The total acidity of water extracts along the soil profile shows a clear picture with relatively small variations (Fig. 3.5).

Acidity maxima were found at 45-50 cm depth, just below the pyrite-jarosite boundary, in columns with low groundwater and a peaty layer on the surface; about 10 cm higher without peat (Table 3.4).

The positions of total acidity maxima for both high and low groundwater treatments were higher in the profile compared with the control (Table 3.4). As the evaporation increased, more acidity was developed in the profile and the position of the total acidity maximum moved upward.

Table 3.4 Averaged pH, EC, total acidity of the first 30 cm in the profile of different columns.

Column number	pH	EC mS/cm	Average total acidity mol/m ³
1	4.05	0.95	0.75
2	3.90	1.05	0.89
3	3.92	0.76	0.38
4	4.00	1.15	0.99
5	3.59	1.24	1.27
6	3.49	1.16	1.19
7	3.54	1.08	1.13
8	3.51	1.36	1.77
9	3.31	1.50	5.57
10	3.10	1.98	13.88
11	3.37	1.26	2.94
12	3.64	0.64	0.79
13	3.79	1.14	0.83
14	3.62	1.08	1.04

The frequency distribution of the acidity maxima is shown in Fig. 3.6 for low and high groundwater levels separately. Although there are few data points only, the peak concentrations of soluble acidity in the low groundwater treatments (without peat) appear to be far higher than with high groundwater. The total acidity of surface soil in treatments with a thin layer of peat was less than without peat.

For both groundwater levels, the average soluble acidity over the whole profile is about 3 mol/m^3 ($s = 0.3$).

A comparison between the controls with a jarositic crack and without cracks respectively shows that the subsoil in the column with a crack has a lower pH, but less total dissolved acid than the column without cracks; this may be ascribed to preferential movement of both oxygen and leaching water into the subsoil along the crack under field conditions before the experiment.

3.3.5 Basic cations

In general, the soluble basic cations did not show much variation between treatments at depths of 25 to 55 cm (Fig. 3.5). An increase in soluble non-acid cations was found in surface soil only as the evaporation increased. A sharp decrease in concentrations of non-acid cations was found in soil horizons below 55 cm after 15 weeks (Fig. 3.5). Among the control columns, the surface soil of the cracked core has a higher concentration of basic cations; this is probably due to less leaching water passing through the surface soil near a crack than further away (short circuiting).

3.3.6 Soil moisture

As expected, the soil moisture contents of different layers along the profile increased with depth. In the half ripe subsoil the gravimetric soil moisture content of the lower layers exceeded 100 percent. The moisture distribution showed little variation among treatments. Disturbance of the surface layer allowed this layer to dry out (Fig. 3.5),

but did not appreciably change the soil moisture distribution along the profile. The disturbed layer may not have been thick enough to decrease drastically the evaporation from lower horizons.

3.3.7 Changes of pH and total acidity of water extracts with cumulative evaporation

Average pH and total acidity over the profile

As the evaporation increased, the average pH of water extracts along the profile decreased (Fig. 3.7). In columns with a high groundwater table, the pH decreased slowly with increasing cumulative evaporation. It decreased sharply in columns with low groundwater. About 140 mm of evaporation in low groundwater treatments resulted in an average pH about 3.5. Except in three columns (9, 10 and 11), the average total acidity of water extracts over the profile did not show much variation with time (Fig. 3.8).

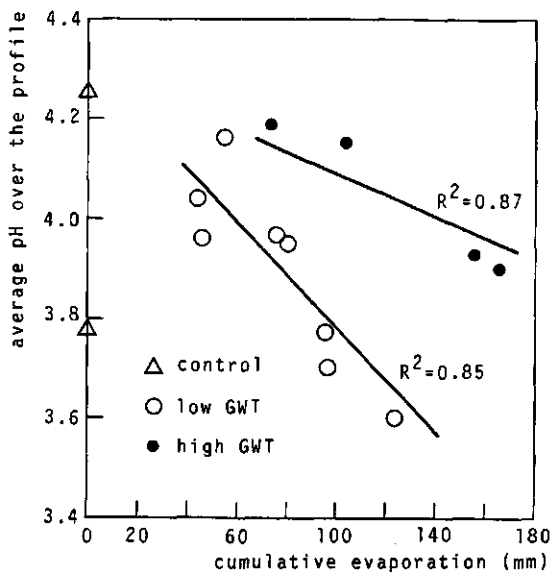


Fig. 3.7 Average pH of extract over the profile in relation to cumulative evaporation.

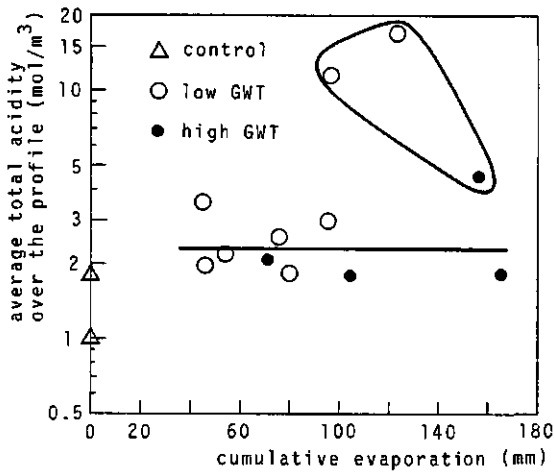


Fig. 3.8 Average total acidity of extract over the profile in relation to cumulative evaporation.

Average pH and total acidity of water extracts in the upper 30 cm

Regardless of groundwater table levels, the average total acidity over the upper 30 cm did not show much variation (Fig. 3.10, Table 3.4). Average pH of surface soil for both groundwater treatments remained 3.5 until the cumulative evaporation exceeded about 100 mm (Fig. 3.9). After that, the pH tended to fall slightly below 3.5.

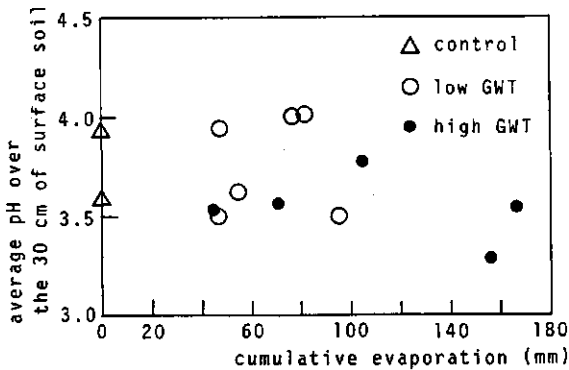


Fig. 3.9 Average pH of extracts over the 30 cm of surface soil in relation to cumulative evaporation.

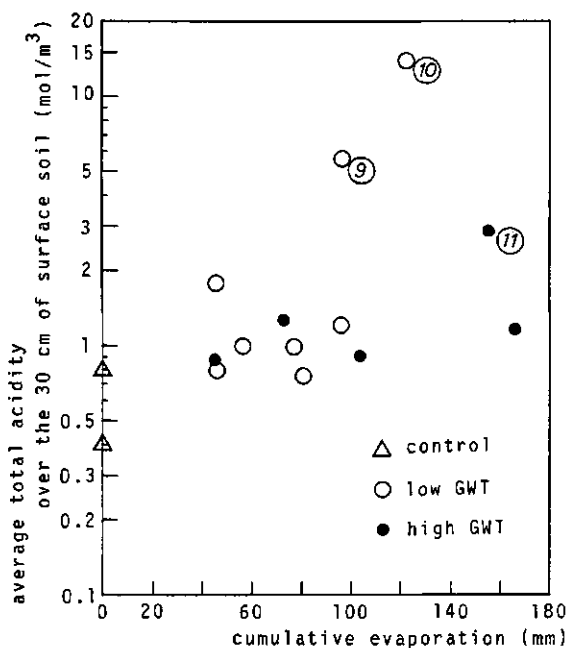


Fig. 3.10 Average total acidity of extracts over the 30 cm of surface soil in relation to cumulative evaporation.

3.3.8 General results and discussion

Average total soluble acidity over the soil profile did not show much variation with cumulative evaporation or with differences in groundwater levels or other factors related to the evaporation rate.

The position and magnitude of the soluble acidity maximum in the soil profile depends on the groundwater table and the presence of peat. A groundwater table below the top of the pyritic layer apparently created conditions enhancing the oxidation of pyritic materials, resulting in high acidity maxima.

Hydrogen ions would be expected to move faster in the soil than Al (or Fe) ions because the diffusion coefficient of hydrogen ion is about three times higher than of Al and Fe.

Changes of average pH over the soil profile with cumulative evaporation depended on groundwater depth. In high groundwater table treatments, pH gradually decreased with cumulative evaporation whereas it decreased sharply where groundwater table was low. The pH of the surface soil only started to drop after about 100 mm of evaporation, in both groundwater levels.

The average pH turned out to be a more sensitive indicator for the development of acidity during the 15-week period of evaporation than the average soluble acid concentration.

With longer periods and higher totals of evaporation, as would occur during the dry season in monsoon climates, pH is expected to become less diagnostic; average soluble acid over the profile and in the surface horizon should then become better indicators for the potential growth of crop plants.

Further research is needed to ascertain the critical amount of evaporation causing unacceptable acidification with different groundwater levels and different depths to pyritic material in the field under different agronomic practices.

Disturbance of 10 cm surface soil only lowered the evaporation rate by about 20 percent. Mulching at the start of the dry season would seem to be a promising management practice in acid sulphate soil, even through its effects in this experiment were small. Further work along this line is needed.

The presence of a peaty layer on the surface reduced the evaporation rate and the total soluble acidity in the soil profile. The peaty layer was relatively dense and slightly platy, however. After ploughing it would have been broken up and incorporated in the Ap horizon.

Because of the local variability of acid sulphate soils, only gross differences become apparent by traditional small-sample methods.

The variability, as shown by the data in this study, consists of two parts: a limited variation about a mean, and some outliers indicating extremely acid, toxic or potentially toxic conditions. Therefore, sampling methods based on bulking even large numbers of subsamples do not fairly represent conditions in most of the soil mass.

Sampling methods should either be based on extensive replication, or depend on close observation and recording of soil differences over small distances, with interpretation of individual results in relation to the observed characteristics of each sample or profile. In both cases, efforts should be made to estimate the frequency distribution of the different values encountered.

The present experiment represents about one month of unchecked evaporation from soils with shallow groundwater during the dry season of a monsoon climate. Therefore, it only shows the beginning of the acidification that bedevils rainfed wetland crop production on acid sulphate soils in such climates.

It is clear, however, that even at relatively low evaporation rates, a groundwater table below the top of the pyritic layer is far more dangerous than a high groundwater table, although this tends to accelerate evaporation and transport of existing acidity to the surface horizon.

Minimizing evaporation during the dry season appears to be the next most important management measure if acidification is to be minimized.

Acknowledgement

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4 EFFECTS OF ACID SULPHATE FLOODWATER ON THE GROWTH OF RICE
AND ON THE CHEMICAL CHANGES IN THREE ACID SULPHATE SOILS.

Abstract

The one-time and cumulative effects of acid sulphate floodwater on the growth of rice and on the chemical changes in three acid sulphate soils were investigated in two successive pot experiments. The pH of acid sulphate floodwater was varied from 3.5 to 5.9, aluminium concentration from 0 to 300 mg/l and iron from 0 to 500 mg/l. These values are representative for floodwater draining from acid sulphate areas in Vietnam. Pots contained 3.5 kg soil and were planted with 2 seedlings of 21-day-old IR36. The experiments were replicated 3 times.

The responses of three acid sulphate soils to added acid sulphate floodwater were different in magnitude but similar in direction of change of various chemical parameters. pH in acid sulphate floodwater alone did not affect the chemical changes of three acid sulphate soils; whereas the presence of Al^{3+} and Fe^{2+} in acid sulphate floodwater produced low pH and enhanced the solubility of Fe.

The pH of acid sulphate floodwater alone as low as 3.5 showed no effect on the growth of rice at early stage. Dry matter yields were negatively correlated with the applied Fe^{2+} and Al^{3+} . High Al^{3+} and Fe^{2+} concentrations in acid sulphate floodwater increased the Al^{3+} and N contents in plants and decreased their Mn content.

Total acid input from the floodwater per unit area was estimated from amount applied, Al^{3+} and Fe^{2+} concentrations and pH. This variable was negatively correlated with dry matter yield and could be used to predict the yield reduction due to acid sulphate floodwater provided that the chemical composition of soil solutions did not reach limiting toxicity levels.

4.1 Introduction

During the rainy season, floodwater in the Mekong Delta flows gently. As it passes over acid sulphate soils, the water collects considerable amounts of acid and other chemicals. The floodwater is fairly acid at the beginning of the rainy season, becomes more acid with time and then becomes nearly neutral. When the acid floodwater flows over the slightly acid sulphate and normal soils of nearby areas it causes poor rice yields and changes soil properties. And when the acid floodwater reaches the river through surface runoff it pollutes the river water. Farmers in some areas use this polluted water to irrigate their field during some parts of the cropping season.

The chemical properties of acid sulphate water vary from place to place (Table 4.1). Its acidity is due to the presence of aluminium and ferric sulphate and sometimes of free sulfuric acid. High aluminium and iron concentrations in water may adversely affect rice plants. Rice was not affected at pH as low as 3.5 in the culture solution at the vegetative stage (Tharwornwong and van Diest, 1974) but suffered from toxicities at 25 to 40 ppm of water soluble aluminium (Cate and Sukhai, 1964; IRRI, 1964) and at about 500 ppm of water soluble iron (Ponnamperuma, 1955).

The objectives of this paper are: a) to study the effects of acid sulphate floodwater on the chemical changes of three acid sulphate soils, and b) to determine whether the acid sulphate water has adverse effects on rice.

Table 4.1 Composition of acid sulphate water at various locations in Vietnam ^{a/}.

Site	pH	Content mg/l			
		SO ₄ ²⁻	Cl ⁻	Al ³⁺	Fe ²⁺
Groundwater at Haiphong expt. station	4.6-7.0	400-1800	400-1800	0-0.58	0-543
Binh luc, Nam ha	5.9	320	-- ^{b/}	-	-
Kinh Thang	2.4	13000	1110	-	-
Vam Co Tay River	3.9-7.0	-	-	-	-
Groundwater Vam Co Tay	2.0	-	-	0-456	0-453
Stagnant water in some ponds	2.5-3.0	2000	-	500-800	-
Few places (not specified)	2	-	-	1000-1500	-

^{a/} Le van Can; personal communication. Such waters are used for irrigation of rice if their pH exceeds 3.5 when fresh water is not available.

^{b/} not determined.

Table 4.2 Chemical properties of three acid sulphate soils.

	Soil type		
	Sinacaban	Leganes (Iloilo)	Aparri
pH (1.1)	3.95	3.90	3.93
EC	39.5	8.49	19.1
%C(%)	5.86	1.55	4.46
N(%)	0.31	0.11	0.34
CEC	14.90	30.9	36.80
Active Fe(%)	5.3	3.0	4.02
Mn(%)	126.0	0.001	179.0
Available P (ppm)	5	2	1

4.2 Materials and methods

Three acid sulphate soils from the Philippines were used. Their chemical properties are listed in Table 4.2. Four-liter pots, with glass tubes at the bottom for drawing out the soil solution, were filled with 3.5 kg air dried soil. The soils were leached with demineralized water to bring the EC of the soil solution to less than 1 mS/cm. Fifty mg/kg of N, P and K were incorporated in the upper few cm. Different kinds of acid sulphate floodwater, depending on the treatments, were applied on wet soils and recycled 5 times to move of the fertilizer down in the soil. The different compositions of acid sulphate floodwater are listed in Table 4.3. These were made with Al_2SO_4 or NaOH. Twenty-one-day-old IR36 seedlings were transplanted. Soil solutions were collected in test tubes previously flushed with nitrogen gas, before and just after transplanting, then once a week for 5 weeks and biweekly thereafter. The solutions were analyzed for Al^{3+} , Fe^{2+} , Ca^{2+} , Mg^{2+} and K^+ up to 8 weeks after transplanting.

The pH of surface water and soil solutions was measured directly by pH meter. The soil solutions were acidified with a few drops of 6 N HCl to prevent oxidation of Fe^{2+} and Mn^{2+} . Subsequent analyses of the acidified solutions were made. Al^{3+} , Fe^{2+} , Ca^{2+} , Mg^{2+} , K^+ and Na were determined directly by atomic absorption spectrophotometer.

Plants observations every week monitored Al^{3+} and Fe^{2+} toxicity symptoms. Plant heights were measured weekly. Eight weeks after transplanting the plants were cut and their dry matter weights recorded. Plant samples were dried at 80°C for 48 hours, ground, stored in polyethylene bags, and redried before analysis. Nitrogen was determined by wet digestion with H_2SO_4 according to the micro-Kjeldahl method (Yoshida and others, 1976). P was determined colorimetrically by the vanadomolybdo-phosphoric acid yellow-method after dry ashing 4 hours at 490°C (Yoshida, 1976); Mn^{2+} , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Fe^{2+} , and Al^{3+} were determined by atomic absorption spectrophotometry after digestion in ternary acid mixture (HNO_3 , H_2SO_4 and HClO_4).

Table 4.3 Compositions of acid sulphate floodwater (ASFW) in the different treatments.

Treatment no.	Content mg/l		
	pH	Al ³⁺	Fe ²⁺
1	3.8	0	0
2	3.8	50	0
3	3.8	100	0
4	3.8	300	0
5	3.8	0	100
6	3.8	50	100
7	3.8	100	100
8	3.8	300	100
9	3.8	100	500
10	4.4	0	0
11	4.4	50	0
12	4.4	0	100
13	4.4	50	100
14	4.4	0	500
15	4.4	50	500
16	5.0	0	0
17	5.0	0	100
18	5.0	0	500
19	5.0	50	500
20	3.5	0	0
21 ^{a/}			

a/ Demineralized water was used

4.3 Results and discussion

4.3.1 Effect of acid sulphate floodwater on the chemical changes of acid sulphate soils during the early growth period of rice

4.3.1.1 Effect of pH of floodwater

The influence of acid sulphate floodwater on the chemical properties of acid sulphate soils varied from soil to soil and season to season (Figs. 4.1-4.9). None of the soils showed any marked difference in the chemical properties of their soil solutions by varying only the pH of the floodwater (Figs. 4.1-4.3). Low pH in association with high aluminium and iron concentrations in acid sulphate floodwater resulted in

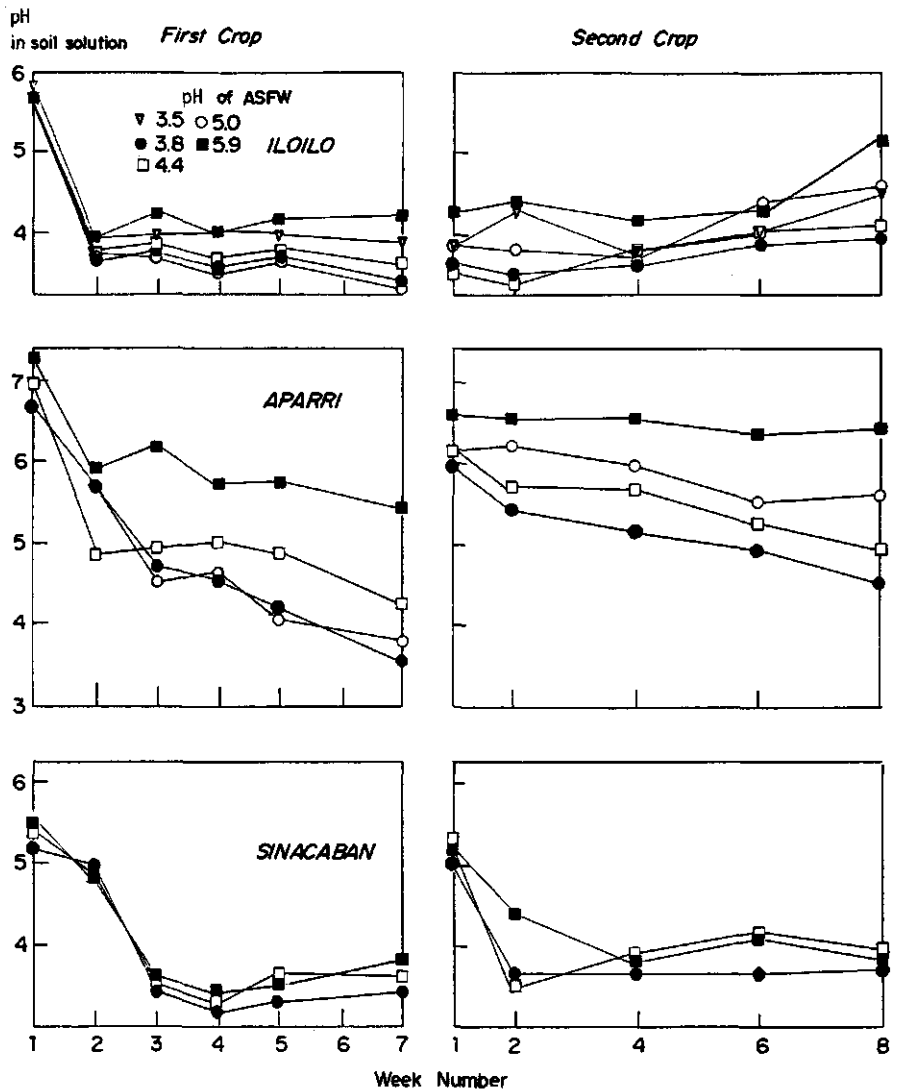


Fig. 4.1 Effect of pH over aluminium and iron in acid sulphate flood water on the changes of pH in the soil solutions of three acid sulphate soils for two cropping seasons; IRRI, 1981.

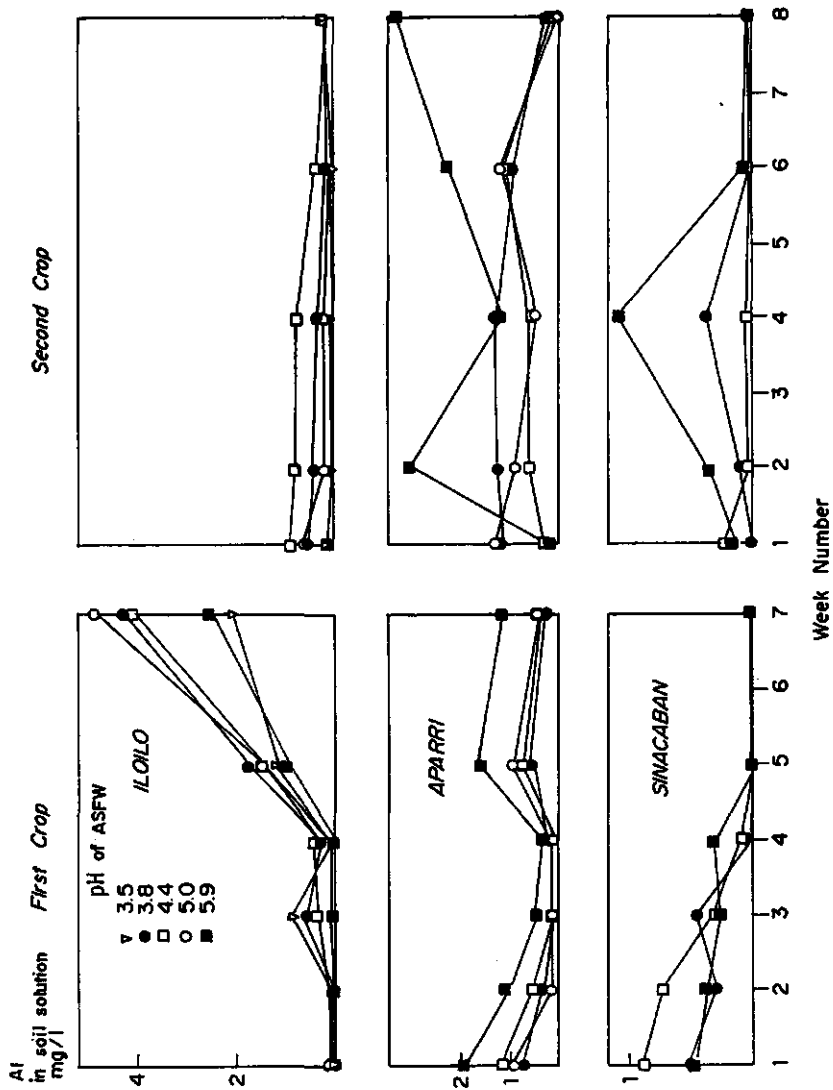


Fig. 4.2 Effect of pH over aluminium and iron in acid sulphate flood water on the changes of aluminium concentrations in the soil solutions of three acid sulphate soils for two cropping seasons; IRRI, 1981.

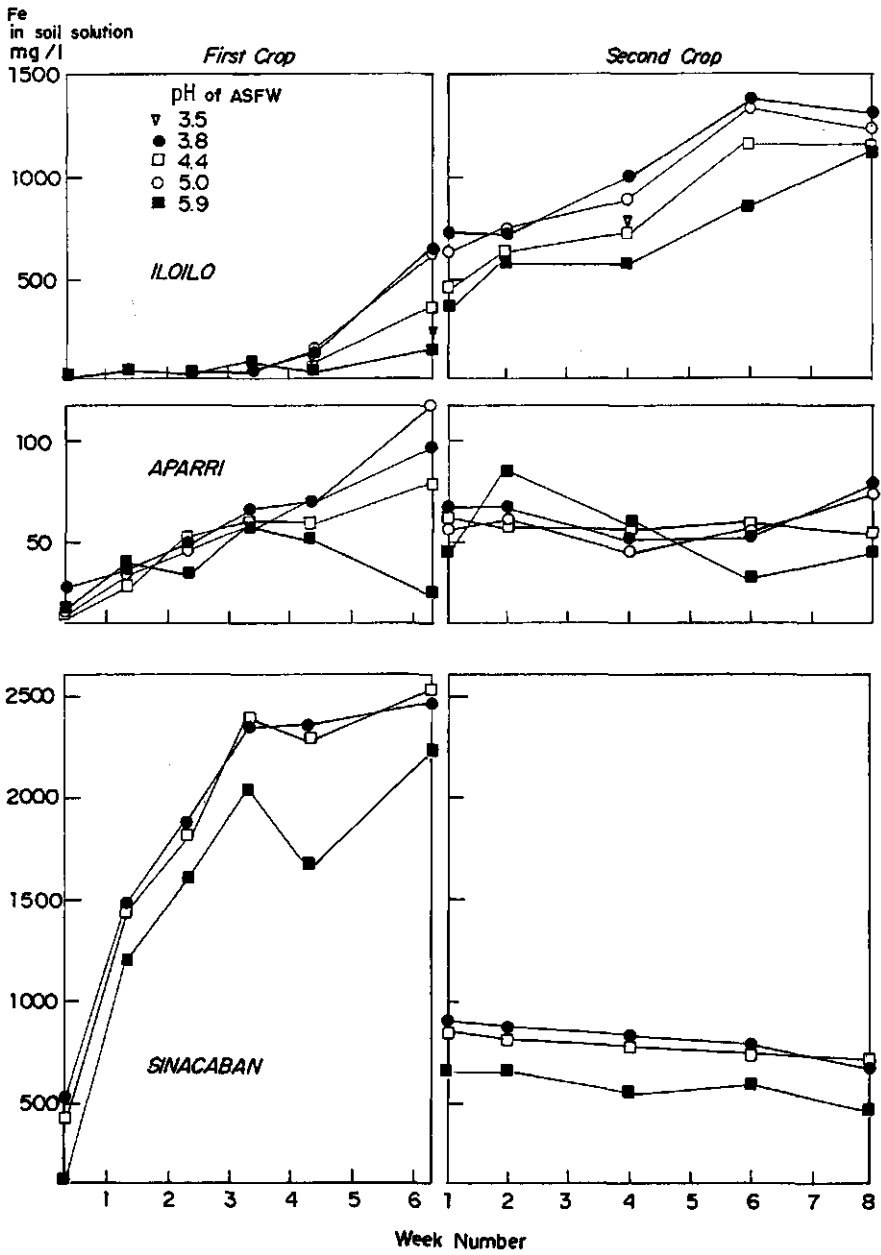


Fig. 4.3 Effect of pH over aluminium and iron in acid sulphate flood water on the changes of iron concentrations in the soil solutions of three acid sulphate soils for two cropping seasons; IRRI, 1981.

a lower pH and higher concentrations of iron in the soil solutions (Figs. 4.1-4.3).

The decreasing concentrations of iron in the soil solutions for Aparri and Sinacaban and the increasing concentration in the soil solution for Iloilo soils during the second crop indicated the difference in the chemical properties of three soils (Figs. 4.1-4.3). Both seasons, low pH in acid sulphate floodwater produced low pH in the soil solutions of all three soils (Fig. 4.1). The higher values of pH starting from transplanting of the second crop were because the soils experienced a month of water-saturated fallow, in which demineralized water was added a few times to compensate for evaporation loss when pots were not closed tightly with a plastic cover. The increase of iron concentrations in soil solutions during the early growth period of rice on Sinacaban and later in Iloilo acid sulphate soils was due to increasing Fe solubility by chemical reduction (Ponnamperuma, 1955).

Regardless of pH and seasons, Al^{3+} concentration in the soil solution showed no variation (Fig. 4.2) because of the high adsorption capacities of soils and the uptake of Al^{3+} by the rice plant.

4.3.1.2 Effects of iron concentration in acid sulphate floodwater

During the first crop, acid sulphate floodwater produced a) a decrease in pH levels (Fig. 4.4), b) no marked effect on the concentration of Al^{3+} in Aparri and Sinacaban soils and a slight increase in the concentration of Al^{3+} in Iloilo soil (Fig. 4.5), and c) an increase in concentration of Fe^{2+} with time (Fig. 4.6) irrespective of Fe levels.

Throughout the period of observations, high concentration of Fe in the acid sulphate floodwater produced low pH in the soil solution (Fig. 4.4), irrespective of soils. The concentration of iron in the soil solutions varied from soil to soil (Fig. 4.5). Sinacaban soil had a markedly high concentration of iron in the soil solution, which was toxic to rice plants, whereas Fe^{2+} concentrations in Aparri and Iloilo did not reach a toxic level at transplanting time of the first crop.

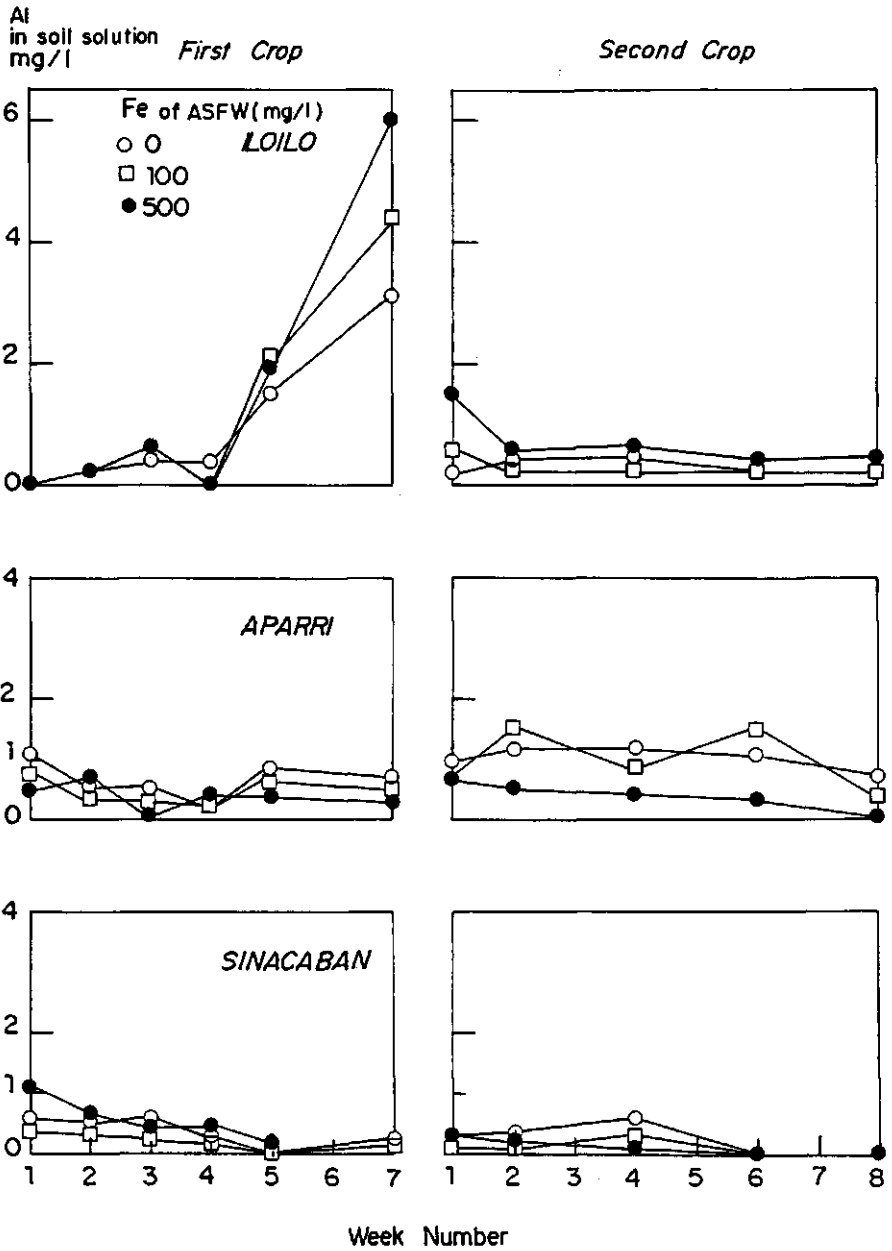


Fig. 4.6 Effect of iron over pH and aluminium in acid sulphate flood water on the changes of aluminium concentrations in the soil solution of three acid sulphate soils for two cropping seasons; IRRI, 1981.

Iron in acid sulphate floodwater contributed to the high acidity in the soil by the oxidation of FeSO_4 and the subsequent release of H_2SO_4 into the soil solution.

During the second crop, the trend in the chemical composition of the soil solutions differed from the first crop. The pH of Iloilo soil gradually increased with time, while there was a slight decrease in pH 2 weeks after transplanting in the Sinacaban and Aparri soils, respectively (Fig. 4.4). The Aparri and Sinacaban soils had a slight increase in the concentration of Fe^{2+} , whereas the Iloilo soil showed a gradual increase in Fe^{2+} concentration (Fig. 4.5). A little variation in Al^{3+} in the soil solutions was observed in Aparri and Sinacaban soils (Fig. 4.6) regardless of iron concentrations in acid sulphate floodwater.

Both seasons, the higher concentration of Fe^{2+} in the acid sulphate floodwater produced lower pH and enhanced the release of iron in the soil solution.

The decrease in pH and increase in Fe^{2+} concentrations in the soil solutions of the Iloilo soil may have been due to the strong chemical reduction process, which dominated the reactions of acid sulphate floodwater.

4.3.1.3 Effects of Aluminium

The influence of Al^{3+} in acid sulphate floodwater on the chemical changes of three acid sulphate soils showed the same trend as of Fe^{2+} for the first and second crops (Figs. 4.7-4.9). As the levels of Al^{3+} in acid sulphate floodwater increased, the pH of the soil solutions decreased, the concentrations of Fe^{2+} increased (Figs. 4.7-4.9) and the concentrations of Al^{3+} did not change.

The higher concentration of Fe^{2+} in the soil solution was due to the increasing solubility at low pH (Ponnamperuma, 1955). The general con-

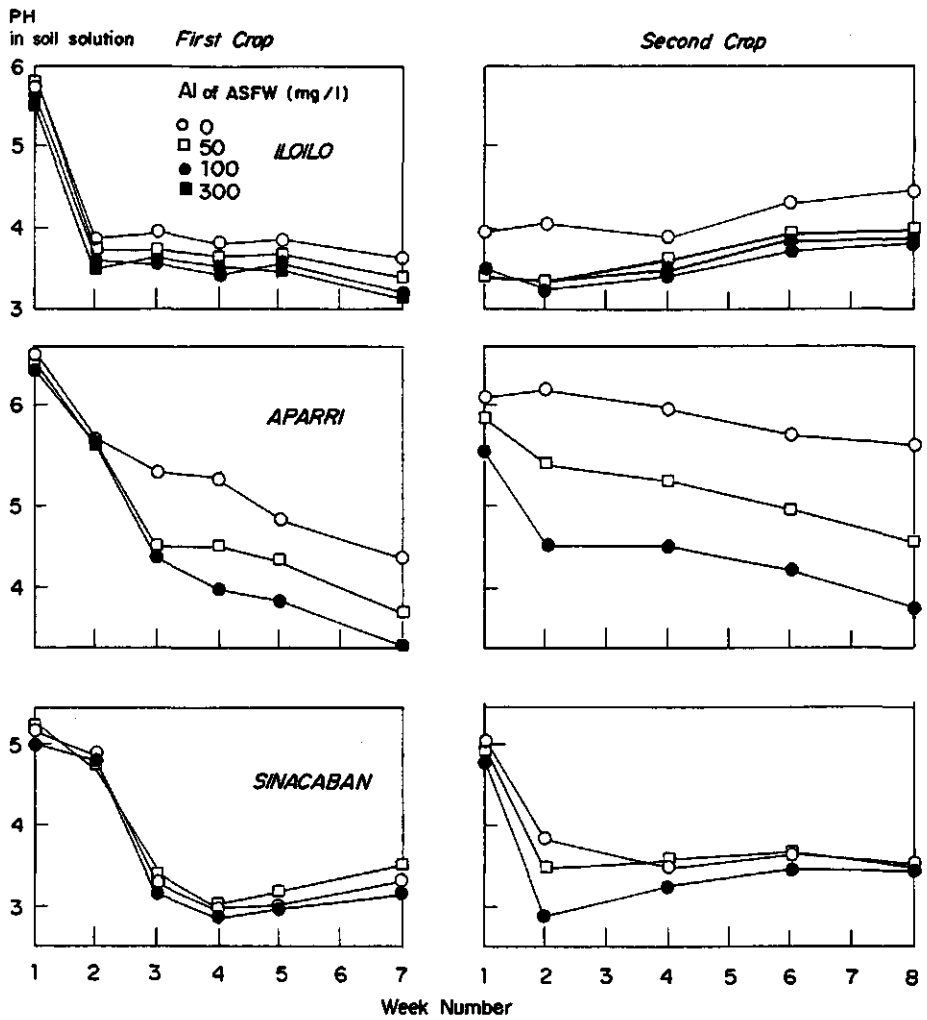


Fig. 4.7 Effect of aluminium over pH and iron in acid sulphate flood water on the changes of pH in the soil solutions of three acid sulphate soils for two cropping seasons; IRRI, 1981.

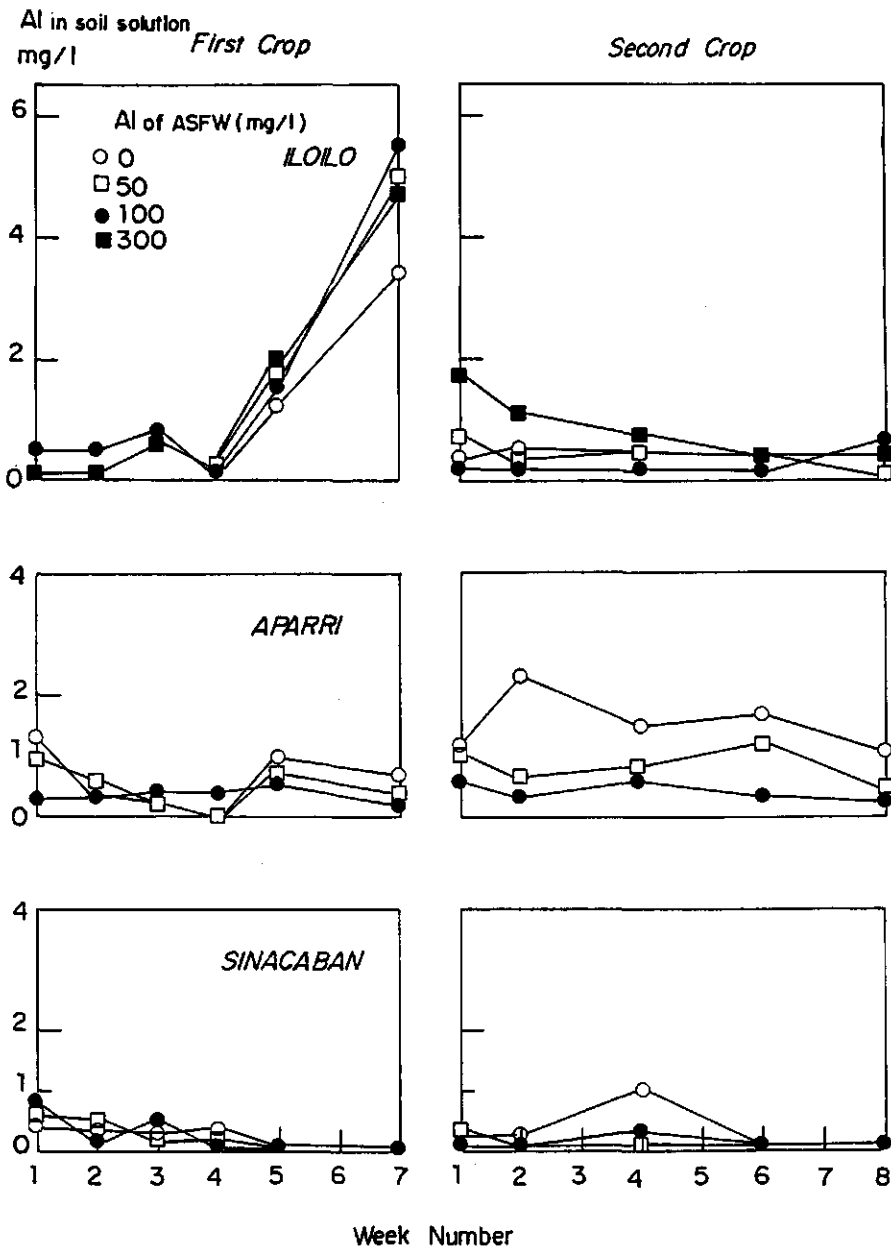


Fig. 4.8 Effect of aluminium over pH and iron in acid sulphate flood water on the changes of aluminium concentration in the soil solutions of three acid sulphate soils for two cropping seasons; IRRI, 1981.

Fe
in soil solution *First Crop*
mg/l

Second Crop

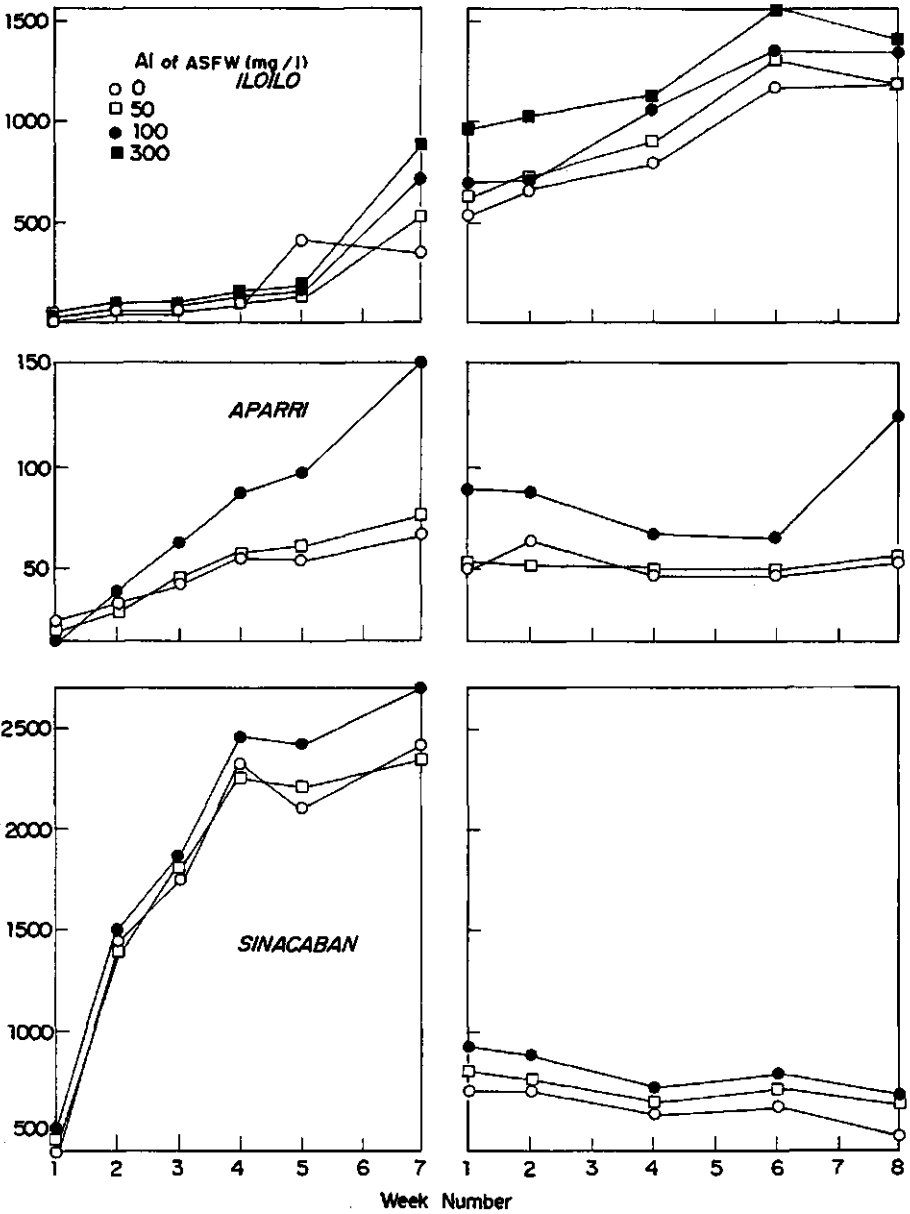


Fig. 4.9 Effect of aluminium over pH and iron in acid sulphate flood water on the changes of iron concentrations in the soil solutions of three acid sulphate soils for two cropping seasons; IRRI, 1981.

stancy of Al^{3+} concentrations in the soil solution was presumable due to the buffering capacity of the soil system.

4.3.2 Effects of acid sulphate floodwater on plant dry matter yield and chemical compositions of IR36 on three acid sulphate soils for two seasons

4.3.2.1 First crop

Eight weeks after transplanting, the plants were harvested, dried and weighted. Dry matter (DM) yields are presented in Table 4.4. Low pH and high iron concentration in the soil solution of Sinacaban acid sulphate soil (Fig. 4.10) resulted in the poorest DM yield among the three soils (Table 4). Rice suffered severe iron toxicity one week after transplanting for all treatments of Sinacaban soil and there was no significant difference in DM yield.

A distinct trend in plant DM yield was observed in Aparri and Iloilo acid sulphate soils (Table 4.4). Lower pH (3.8) in association with high Al^{3+} and Fe^{2+} concentrations in acid sulphate floodwater caused a decrease in yield. The greater effect of Al^{3+} on plant DM is seen in Fig. 4.10. DM yield decreased sharply as the concentrations of Al in acid sulphate water increased. In contrast, Fe^{2+} concentrations in acid sulphate floodwater up to 100 mg/l did not influence DM yield. The effect of Fe^{2+} on DM yield showed little variation.

The chemical composition of IR36 at 8 weeks after transplanting under the influence of pH, Al^{3+} , and Fe^{2+} of acid sulphate floodwater is presented in Table 4.5. The content in plants was slightly affected by changes in pH of the acid sulphate floodwater applied. At low pH, plants tend to absorb more N in the form of ammonium, and less metallic cations (Table 4.5). The concentrations of N and Al^{3+} in plants increased as levels of Al in the solution increased whereas the Mn content showed the reverse (Table 4.5). The high concentrations of Al^{3+} in plants as levels of Al^{3+} in acid floodwater increased may be due to the high absorption capacities of plants. The concentration of P, Fe^{2+}

Plant dry matter yield (g/pot)

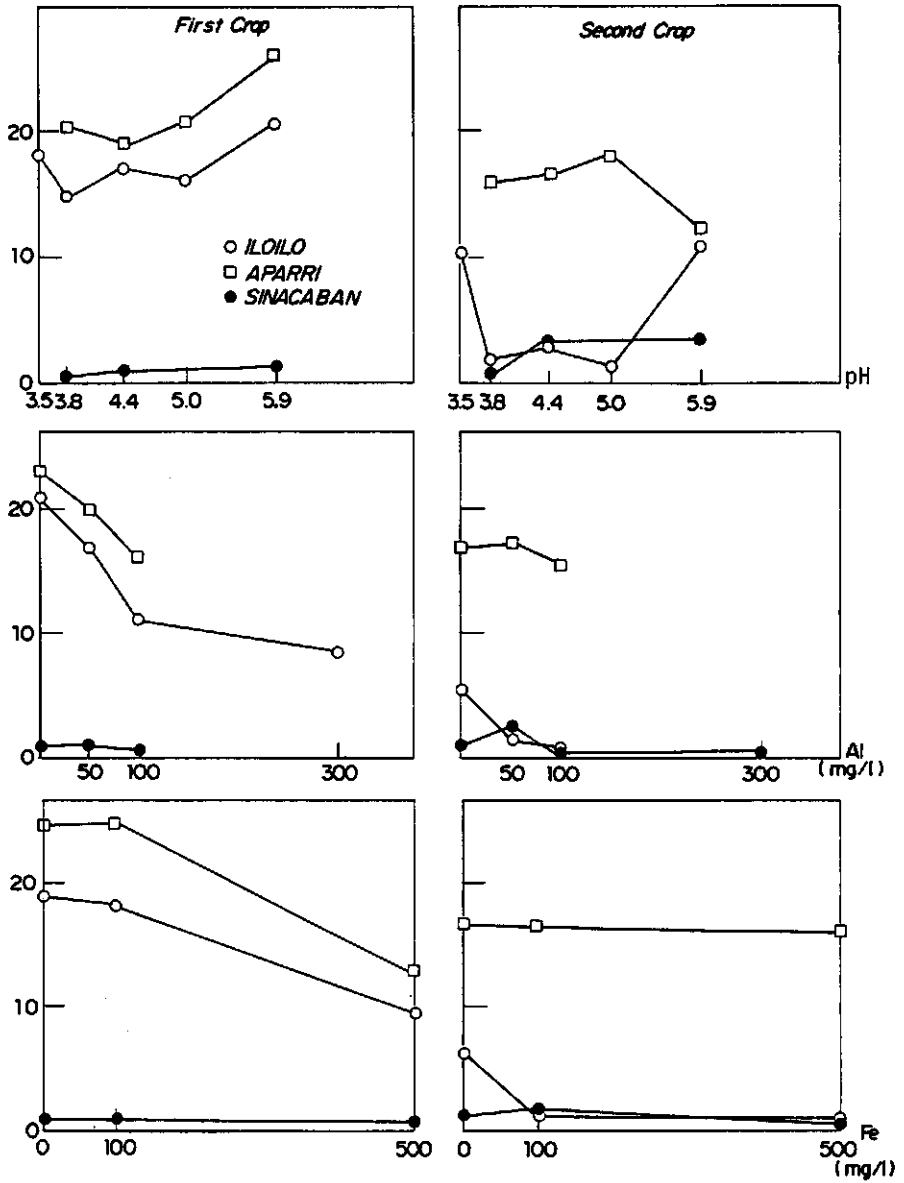


Fig. 4.10 Effect of pH, aluminium and iron in acid sulphate flood water on plant dry matter yield of IR36 in three acid sulphate soils for two cropping seasons; IRRI, 1981.

Table 4.4 Effect of different combination of acid sulphate floodwater on the plant dry matter yield of IR36 on three acid sulphate soils for two cropping seasons, IRR1, 1981.

Treat ment no.	Treatment		Mean plant dry matter yield (g/pot)					
	pH	mg/l	First crop			Second crop		
			Sinacaban	Aparri	Iloilo	Sinacaban	Aparri	Iloilo a/
1	3.8	0	0.46 b	24.39 ab	22.82 a	0.18 d	18.40 ab	11.17 a
2	3.8	50	0.46 b	20.42 bcd	21.58 ab	1.72 cd	18.70 a	0.48 f
3	3.8	100	0.27 b	16.91	def 10.41 d	0.15 d	17.0 ab	0.61 ef
4	3.8	300	0		7.93 de			0.01 f
5	3.8	0	0.47 b	25.61 ab	21.16 ab	0.01 d	15.46 abc	3.43 cdef
6	3.8	50	0.52 ab	22.95 abc	19.22 bc	0.01 d	16.33 ab	0.03 f
7	3.8	100	0.57 ab	17.65 cde	16.17 c	0.38 cd	15.03 bcd	0.38 f
8	3.8	300	100		8.85 de			0.15 f
9	3.8	100	0.40 b	13.29	ef 6.64 de	0.01 d	19.98 d	0.01 f
10	4.4	0			22.76 ab			6.36 abcde
11	4.4a	50	0.54 ab	23.22 ab	20.52 ab	3.31 bc	16.16 ab	7.81 abc
12	4.4	0			19.53 abc			1.80 def
13	4.4a	0	1.07 a	22.06 abc	19.11 bc	7.45 a	16.23 ab	0.43 f
14	4.4	0			9.95 d			0.15 f
15	4.4	50	0.40 b	12.19	f 8.34 de	0.01 d	18.02 ab	0.07 f
16	5.0	0			21.46 ab			6.44 abcd
17	5.0	0			22.17 ab			4.87 bcdef
18	5.0	0			ef 10.71 d			0.18 f
19	5.0	50			8.98 de			0.04 g
20	3.5	0			17.97 bc			10.24 ab
21	5.9	0	0.83 ab	26.59 ab	20.59 ab	3.53 b	12.28 cd	11.01 ab

a/ Any two means dry plant matter yield in the same column with the same letter are not significantly different at 5% level by Duncan Multiple range test.

Table 4.5 Effects of pH^{a} , $\text{Al}^{3+\text{b}}$ and $\text{Fe}^{2+\text{c}}$ of acid sulphate floodwater on the chemical composition of IR36 plant in Aparri and Iloilo acid sulphate soils, first crop, IRRI, 1981.

pH level	Soil						Aparri						Iloilo					
	N (%)	P (%)	K (%)	Na (%)	Mg (%)	Ca (%)	Al ppm	Fe ppm	Mn ppm	N (%)	P (%)	K (%)	Na (%)	Mg (%)	Ca (%)	Al ppm	Fe ppm	Mn ppm
3.5										1.75	0.25	3.33	0.17	0.15	0.15	63	113	54
3.8	2.08	0.19	3.08	0.46	0.21	0.16	38	96	243	2.26	0.26	3.61	0.22	0.17	0.15	82	149	25
4.4	2.21	0.18	3.16	0.42	0.21	0.16	44	132	279	2.02	0.26	3.60	0.23	0.18	0.14	39	145	46
5.0	2.08	0.18	3.13	0.46	0.21	0.18	27	137	340	2.14	0.26	3.61	0.28	0.17	0.14	38	152	29
5.9	1.68	0.21	3.06	0.36	0.22	0.20	33	106	320	1.32	0.24	3.32	0.13	0.18	0.16	32	105	54
Al level (mg/l)																		
0	1.85	0.19	3.07	0.44	0.21	0.17	30	112	352	1.72	0.26	3.55	0.18	0.17	0.15	40	121	40
50	2.05	0.18	3.14	0.43	0.21	0.16	42	115	284	2.04	0.25	3.45	0.25	0.17	0.14	45	150	36
100	2.94	0.19	3.12	0.50	0.22	0.17	45	112	115	2.66	0.26	3.70	0.33	0.19	0.14	61	181	13
300										3.30	0.29	3.99	0.44	0.17	0.14	179	181	8
Fe level (mg/l)																		
0	1.84	0.19	3.13	0.45	0.22	0.18	37	86	286	1.78	0.24	3.52	0.19	0.17	0.15	55	105	46
100	1.95	0.19	3.05	0.43	0.22	0.17	36	96	344	1.80	0.25	3.44	0.22	0.17	0.14	66	124	37
500	2.77	0.17	3.15	0.48	0.18	0.14	36	196	52	3.08	0.30	3.90	0.40	0.19	0.14	45	277	10

a/ Averaged over Al^{3+} and Fe^{2+} treatments

b/ Averaged over pH and Fe^{2+} treatments

c/ Averaged over pH and Al^{3+} treatments

Table 4.6 Effects of pH^{a/}, Al^{3+b/}, and Fe^{2+c/} of acid sulphate floodwater on the chemical composition of IR36 plant in Aparri and Iloilo acid sulphate soils, second crop, IRRI, 1981.

pH level	Soil						Aparri						Iloilo					
	N (%)	P (%)	K (%)	Na (%)	Mg (%)	Ca (%)	Al ppm	Fe ppm	Mn ppm	N (%)	P (%)	K (%)	Na (%)	Mg (%)	Ca (%)	Al ppm	Fe ppm	Mn ppm
3.5	1.37	0.23	1.96	0.56	0.21	0.18	22	65	174	1.91	0.29	2.70	0.42	0.18	0.12	18	252	34
3.8	1.32	0.24	1.88	0.60	0.22	0.16	11	74	238	2.80	0.29	2.52	0.59	0.19	0.12	48	436	21
4.4	1.27	0.24	1.67	0.65	0.21	0.13	12	70	190	2.61	0.27	2.55	0.51	0.18	0.12	23	354	27
5.0	1.23	0.26	1.72	0.55	0.21	0.14	9	63	96	2.31	0.31	2.72	0.51	0.18	0.12	11	344	28
5.9										1.62	0.28	2.73	0.32	0.18	0.14	8	490	53
Al level (mg/l)																		
0	1.25	0.25	1.7	0.63	0.22	0.16	12	66	198	2.40	0.30	2.70	0.53	0.19	0.12	17	403	30
50	1.30	0.23	1.92	0.54	0.22	0.18	14	70	226	2.76	0.26	2.35	0.46	0.17	0.11	49	360	24
100	1.56	0.21	2.11	0.58	0.18	0.14	30	69	93									
300																		
Fe level (mg/l)																		
0	1.18	0.24	1.74	0.57	0.21	0.15	14	58	204	2.25	0.29	2.72	0.46	0.18	0.12	25	344	33
100	1.28	0.25	1.86	0.59	0.23	0.2	18	63	215	2.82	0.40	2.40	0.58	0.18	0.12	26	436	21
500	1.72	0.21	2.13	0.60	0.19	0.14	18	95	99									

a/ Averaged over Al³⁺ and Fe²⁺ treatments

b/ Averaged over pH and Fe²⁺ treatments

c/ Averaged over pH and Al³⁺ treatments

and other cations was not influenced by Al^{3+} . A similar trend was found for N, Fe^{2+} , and Mn^{2+} in plants as the level of Fe in acid sulphate floodwater increased (Table 4.5).

4.3.2.2 Second crop

The plant DM yields of different treatments for three soils are presented in Table 4.4. In general, DM yields were lower than the first crop because of weather and of the cumulative effects of acid sulphate floodwater prevailing during the first and second crops.

At transplanting, low pH and high Fe^{2+} in the soil solutions of Sinacaban caused toxicities to rice plants. No significant difference in DM yields was seen among treatment means (Table 4.4). The slight variation in plant dry matter yield among treatments of Aparri acid sulphate soils was due to no marked difference in pH and Fe^{2+} concentrations in the soil solutions.

In Aparri soil, the DM weight was not affected by the levels of Fe^{2+} whereas the Fe^{2+} treatment showed a sharp decrease in DM yield in Iloilo soils at 100 mg/l. A pH range from 3.5 to 5.9 alone did not significantly affect the plant dry matter yield in Iloilo acid sulphate soils because at transplanting the Fe^{2+} concentration in the soil solutions was less than 500 ppm (Fig. 4.3). Other treatments at Iloilo showed Fe^{2+} toxicity symptoms a few weeks after transplanting because of the high concentrations of iron in the soil solution. The DM yield, therefore, dropped to minimal values.

The trend of the chemical compositions of plant materials was similar to the first season (Table 4.6).

4.3.3 Quantitative relationship between acid sulphate floodwater and plant dry matter yield

To quantify the yield reduction due to acid sulphate floodwater, yield was correlated with pH levels and concentrations of Al^{3+} and Fe^{2+} in acid sulphate floodwater. Regression analysis for the first crop showed that the DM yield could be expressed by the following equation:

$$Y = 36.12 - 9.49S - 0.035\text{Al} - 0.015 \text{ Fe } (R^2 = 0.707)$$

where, Y is DM yield (g/pot), S is the dummy variable (S = 1, 2, 3 for Aparri, Iloilo and Sinacaban soils, respectively), Al^{3+} is the concentration of Al^{3+} (mg/l), and Fe^{2+} is the concentration of Fe^{2+} (mg/l) applied in the acid sulphate flood water.

Plant DM yield was strongly influenced by soil type, and negatively correlated with Al^{3+} and Fe^{2+} concentrations in the acid water. A separate regression analysis was also performed for each soil during the first crop. Negative correlation between DM yield and the concentration of Al^{3+} and Fe^{2+} was also found in Aparri and Iloilo soils:

$$\text{Aparri: } Y = 25.27 - 0.057 \text{ Al} - 0.017 \text{ Fe } (R^2 = 0.707)$$

$$\text{Iloilo: } Y = 22.27 - 0.045 \text{ Al} - 0.022 \text{ Fe } (R^2 = 0.844)$$

No correlation was observed for the Sinacaban soil.

During the second crop, DM yield data of Aparri and Iloilo soils were correlated. The variation of DM yield due to Al^{3+} , and Fe^{2+} concentrations in acid sulphate floodwater was:

$$Y = 23.62 - 7.67S - 0.022 \text{ Al} - 0.006 \text{ Fe } (R^2 = 0.676)$$

This could be explained as a decrease in cumulative effects of Al and Fe^{2+} in acid sulphate floodwater when the chemical compositions in the solution reached limiting values.

Plant dry matter yield reduction due to aluminium and iron in acid sulphate flood water could be represented by:

$$Y = 6.14 - 0.022 \text{ Al} - 0.011 \text{ Fe} \quad (R^2 = 0.424) \text{ for Iloilo soil.}$$

Because the acidity of acid sulphate floodwater is attributed to the presence of Al^{3+} , Fe^{2+} sulphates and free sulphuric acid, a single factor was used to calculate the total acidity. The total acidity is the sum in equivalent per liter of three ions: H^+ , Al^{3+} and Fe^{2+} . Because the temperature in the greenhouse was higher than outside, the evapotranspiration was assumed of 10 mm/day and 8 mm/day for the first and second crops. Water added during the recycling fertilizers of the first crop was 80 mm (or 1.5 liters). The cumulative acidity for first and second crops was then calculated by multiplying the amount of added acid sulphate floodwater and its chemical concentrations in equivalents. This factor was used to correlate with the DM yield. Negative correlation between total acidity and DM yield of Aparri and Iloilo acid sulphate soils for the first crop was:

$$Y = 23.45 - 0.04 X \quad (R^2 = 0.742)$$

where y is the DM yield (g/pot) and X is the total acidity in equivalents/l for Aparri and Iloilo acid sulphate soils. Very poor correlation was found for the second crop because high acidity and high Fe concentration in the soil solutions resulted in poor yields. This simple factor could be used to predict the yield reduction provided that certain elements in soil solutions did not reach toxic levels.

4.4 Conclusions

On the basis of these findings the following general conclusions and recommendations can be made:

1. The responses of three acid sulphate soils to added acid sulphate floodwater were different in magnitude but similar in direction of change of various chemical parameters.

2. pH alone did not affect the chemical changes of three acid sulphate soils; Al^{3+} or Fe^{2+} in the acid sulphate floodwater produced low pH and enhanced the solubility of Fe^{2+} .
3. High Al^{3+} concentrations in acid sulphate floodwater caused low pH in the solution through the exchange of Al^{3+} and H^+ in the clay complex.
4. Acid sulphate floodwater did not affect the concentration of Al^{3+} in the soil solution due to the high buffering adsorption capacities of the soils.
5. pH levels of acid sulphate floodwater alone as low as 3.5 showed no effect on the growth of rice at early stage.
6. Plant DM yield was negatively correlated with Fe^{2+} and Al^{3+} concentrations in acid sulphate floodwater for the first and second crops.
7. pH levels are not influenced by the chemical uptake of IR36 whereas the presence of high Al^{3+} and Fe^{2+} concentration in acid sulphate floodwater added to the soils enhanced the Al and N uptake and depressed the Mn.
8. Concentrations of Al^{3+} and Fe^{2+} in the acid sulphate floodwater up to 50 and 100 mg/l, respectively, did not directly influence the growth of rice.
9. The one-time and cumulative effects of acid sulphate floodwater on DM yield varied from soil to soil.
10. A single factor, total acidity, i.e. the sum of H^+ , Al^{3+} and Fe^{2+} in equivalents, could be used to determine the reduction in plant DM yield provided that the chemical compositions of soil solutions did not reach limiting toxicity values.

The experiment was in the greenhouse where the hydrological factors were limited. Field studies are therefore needed to investigate the transformation of acid sulphate floodwater in soils and its influence on rice yield.

effectiveness for a particular soil is determined largely by pH, P and Ca concentrations in the soil solution (Peaslee et al., 1962, Ellis et al., 1955, Khasawneh and Doll, 1978, Graham, 1955 and Howe and Graham, 1957). Many experiments have been conducted to determine the most favourable soil and cropping conditions for its use. In general, experimental results have shown that rock phosphate is more effective on acid soils than on neutral or alkaline soils (Peaslee et al., 1962, Ensinger et al., 1967, Barnes and Kamprath, 1975). The use of acid-forming N sources, or mixing elemental S with rock phosphate results in the solubilization of appreciable amounts of P and, generally, in better yields (Volk, 1944).

In acid sulphate soils (and acid lateritic soils), rice responded favourably to rock phosphates (Le van Can, 1982, La thi Hien and Vo tong Xuan, 1979, and Misra and Panda, 1969). Incubating rock phosphate under moist conditions for three weeks before transplanting produced better rice yields than application just before transplanting (Shinde et al., 1978).

Phosphorus deficiency is widespread in rice and other crops in many tropical countries. Only nitrogen deficiency appears to be more extensive. In acid sulphate soils, however, phosphorus is the main limiting macronutrient for crop production.

Since the use of superphosphate is a luxury in many developing countries because of their limited foreign exchange, direct application of ground rock phosphate from local deposits may be an economic alternative for P fertilization.

5.2 Objective

The objective of this study was to study the response of rice to different phosphate sources and fertilization methods on surface horizon material of two acid sulphate soils.

5.3 Materials and methods

Material from the surface horizons of two acid sulphate soils, from Iloilo and Malinao, The Philippines, was used in this experiment. Their chemical properties are shown in Table 5.1.

Table 5.1 Some chemical characteristics of the two surface horizon materials.

Chemical characteristics	Material	
	Malinao	Iloilo
pH of dry soil (1:1 H ₂ O)	3.50	3.90
ECe (mS/cm)	1.0	8.49 (2.0) ¹⁾
CEC (mmol/100 g)	2.5	30.9
organic C (%)	1.23	1.55
Total N (%)	0.15	0.11
Active Fe (%)	2.50	3.0
Active Mn (%)	0.001	0.001
Exch. K (mmol/100 g)	0.17	-
Exch. SO ₄ ²⁻ (%)	0.27	-
Olsen P (ppm)	5.8	2.0 (15.0) ¹⁾

¹⁾ First value for material as sampled; value in brackets for material after leaching for 1 week.

The soil from Iloilo was leached with demineralized water to bring down the salinity level. Two sources of 100 mesh rock phosphate were used: Lumpoon from Thailand (5.8% P₂O₅) and North Carolina (30% P₂O₅) rock phosphate.

Six kg soil was placed in a 12 litre plastic pot. All pots received uniform rates of 50 ppm N and K as urea and potassium chloride. Then, phosphate was applied (except to controls) and the soil was well mixed. One set of triplicates was brought to 60-70% of field capacity, another set to field capacity. These were incubated for three weeks. A third set of triplicates was not incubated. The treatment combinations are listed in Table 5.2.

Table 5.2 Treatment combinations of different phosphate rates and fertilizing times and methods.

<u>Fertilizing time and method</u>				
time before transplanting		3 weeks	3 weeks	1 day
water status		2/3 FC ¹⁾	FC	flooded
P rate				
source	ppm P			
control	0			X
SP ²⁾	50			X
RP ³⁾	50	X	X	X
	100	X	X	X

1) 2/3 FC: 60-70% of field capacity

2) SP : superphosphate

3) RP : rock phosphate

The soils in all pots were then flooded, puddled, left overnight and four rice seedlings, 21 days old, cv. IR 36 were transplanted. After 30 days, two of the seedlings were cut and dried for chemical analysis. At maturity, the other two plants in each pot were harvested and oven-dry weights of grain and straw were recorded separately. Straw samples were then ground for analysis of N, P, Fe and Al.

Treatments were completely randomized. The significance of differences between treatments was analyzed by Duncan's Multiple Range Test.

5.4 Results and discussion

5.4.1 Effect of variation in phosphate rate, time of fertilizer application and soil moisture status on pH of the soil solution at transplanting and 6 weeks after transplanting

At transplanting, the pH of the soil solution varied only slightly among the treatments (Table 5.3).

Table 5.3 pH of the soil solution at transplanting and 6 weeks after transplanting under different phosphate rates, time of application and soil moisture status on two acid sulphate soils.

time before transplanting		3 weeks	3 weeks	1 day	3 weeks	3 weeks	1 day
water status		2/3 FC	FC	flooded	2/3 FC	FC	flooded
P	rate	Iloilo			Malinao		
source	ppm P						
<hr/>							
		at transplanting					
Carolina RP	50	4.40	4.36	4.15	4.15	4.23	4.12
	100	4.32	4.50	4.27	4.30	4.18	4.25
Lumpoon RP	50	4.43	4.27	4.17	4.32	4.36	4.30
	100	4.39	4.31	4.18	4.43	4.45	4.42
superphosphate	50			4.00			4.02
control	0			4.13			4.17
<hr/>							
		6 weeks after transplanting					
Carolina RP	50	4.05	4.17	4.03	5.07	5.48	5.12
	100	4.18	4.63	4.25	4.90	5.63	5.07
Lumpoon RP	50	4.45	4.60	4.05	5.08	5.55	5.08
	100	4.33	4.68	4.32	4.88	5.60	5.27
superphosphate	50			4.15			5.07
control	0			3.98			5.07

For each soil, values are not significantly different at 5% level by DMRT.

Six weeks later, the pH of the soil solution in the Iloilo soil had not changed in spite of the submergence, except for a slight increase in the rock phosphate treatments. The highest increase in pH of the Malinao soil occurred in treatments where either of the two rock phosphates was incubated at FC for 3 weeks before transplanting (Table 5.3), but even the control increased by 0.9 unit. This may be attributed to the production of alkalinity by reductions during submergence.

5.4.2 Effect of variation in phosphate rate, time of fertilizer application and soil moisture status on grain yield, straw weight, plant height, tiller and panicle numbers

Without P fertilization, Iloilo soil produced a higher grain yield than Malinao (Table 5.4). This was probably due to the high P availability after leaching in the former soil (Table 5.1).

The response of rice to different phosphate rates and application time varied between the two soils (Table 5.4). In the Iloilo soil, the grain yield showed little response to rock phosphate fertilizer. Malinao soil, however, produced the highest yields in treatments where either of the rock phosphates was applied and the soil was kept at field capacity for three weeks before transplanting (Table 5.4). The other application methods (60-70% FC for three weeks, and one day before transplanting) did not show good response to rock phosphate in Malinao soil. Superphosphate was effective, however. In Malinao, there was a significant increase in grain yield with increased application rate of Carolina phosphate, but not of Lumpoon phosphate, in the treatments kept at field capacity three weeks before transplanting.

Irrespective of source, RP application to Malinao soil at FC three weeks before transplanting produced the highest straw weight, plant height and number of panicles (Table 5.4): the same trends as in grain yield.

The higher control yield in Iloilo soil corresponds to the higher Olsen P value compared with Malinao. The lower maximum yields and the lower response to all methods of P application may be related with the persistently low pH, which remained about 4 to 4.5 even after 6 weeks of flooding. In the Malinao soil, the pH had risen about one unit by that time.

Table 5.4 Effect of variation in phosphate rate, time of fertilizer application and soil moisture status on grain yield, straw weight, plant height, tiller number and panicle number of rice plants at harvest in two acid sulphate soils.

time before transplanting		3 weeks	3 weeks	1 day	3 weeks	3 weeks	1 day
water status		2/3 FC	FC	flooded	2/3 FC	FC	flooded
P	rate	Iloilo			Malinao		
source	ppm P						
<u>Grain yield (g/pot)</u>							
Carolina RP	50	24.50 bc	22.15 d	22.28 d	14.09 de	28.89 b	12.08 e
	100	24.54 bc	22.32 d	24.63 b	16.02 d	35.44 a	14.18 de
Lumpoon RP	50	23.54 c	20.99 e	17.58 f	15.13 d	32.91 a	14.78 d
	100	26.33 a	21.24 de	22.18 d	24.14 c	33.38 a	13.06 de
superphosphate	50			22.00 d			29.06 b
control	0			17.84 f			11.34 e
<u>Straw weight (g/pot)</u>							
Carolina RP	50	12.75 a	11.88 ab	11.14 ab	12.81 d	13.58 cd	10.64 f
	100	12.18 ab	11.83 ab	12.01 ab	13.48 cd	15.94 ab	11.02 ef
Lumpoon RP	50	12.40 ab	10.83 bc	9.96 bc	12.00 de	15.02 ab	9.09 g
	100	13.91 a	11.78 ab	11.64 ab	14.78 bc	16.60 a	8.98 g
superphosphate	50			12.24 ab			13.67 cd
control	0			9.74 bc			7.50 h
<u>Plant height (cm)</u>							
Carolina RP	50	80.6 d	80.1 d	76.0 ef	80.5 ef	86.8 bc	69.3 h
	100	80.9 d	80.5 d	78.7 de	83.8 d	89.0 ab	70.5 h
Lumpoon RP	50	85.0 c	76.9 ef	75.3 f	82.2 de	88.9 ab	78.8 f
	100	91.4 a	81.8 d	84.5 c	84.5 cd	89.8 a	76.0 g
superphosphate	50			88.60 b			88.3 ab
control	0			74.6 f			69.0 h
<u>Tiller number</u>							
Carolina RP	50	22.7 ab	20.3 c	19.7 c	21.3 d	28.7 b	17.3 e
	100	24.7 a	20.7 bc	22.3 b	23.0 cd	32.0 a	18.6 e
Lumpoon RP	50	21.7 bc	21.3 bc	20.3 c	18.7 e	27.0 b	17.3 e
	100	23.7 ab	21.7 bc	23.7 ab	22.0 d	30.0 a	13.7 f
superphosphate	50			24.6 a			24.2 c
control	0			19.3 c			15.0 f
<u>Panicle number</u>							
Carolina RP	50	21.0 b	20.3 b	19.3 b	21.0 ef	27.3 b	17.0 h
	100	24.7 a	19.7 b	20.3 b	22.0 c	30.0 a	18.3 gh
Lumpoon RP	50	21.0 b	19.0 b	20.0 b	18.7 fg	24.7 c	15.0 k
	100	22.7 ab	20.3 b	23.7 ab	20.0 f	28.0 b	13.0 l
superphosphate	50			24.3 ab			23.7 d
control	0			18.7 c			15.0 k

For each soil, means having the same letter are not significantly different at 5 percent level by DMRT.

5.4.3 Effect of variation in phosphate rate, time of fertilizer application and soil moisture status on the chemical composition of rice plants during the growing period

One month after transplanting

The concentration of N, Fe and Al in rice plants one month after transplanting showed little variation among the two soils and all treatments (Table 5.5). Only in the Malinao soil, high Fe and Al concentrations occurred in plants from the superphosphate treatment as well as the RP treatment with incubation at FC for 3 weeks before transplanting. The superphosphate treatment and most of the rock phosphate applications with 3 weeks incubation resulted in increased P concentrations in plants. Since P concentrations on Iloilo soil were of the same order as on Malinao, and well above the deficiency range, the lower yields on Iloilo cannot be ascribed to P deficiency in the fertilized treatments.

At harvest

In general, there was little variation in the N, Fe and Al contents of straw at harvest on the Iloilo soil (Table 5.6). P concentrations in straw after rock phosphate application at field capacity were higher than in the other treatments. Concentrations of N, P and Fe in straw on Malinao soil with rock phosphate were higher after incubation at field capacity than at 60-70% FC; concentrations were erratic in treatments without incubation.

5.4.4 Relative agronomic effectiveness of rock phosphate compared with superphosphate

Table 5.5 shows the relative agronomic effectiveness of the different treatments compared with a standard application of superphosphate. In Iloilo soil, Carolina and Lumpoon rock phosphates incubated at 60-70% FC for 3 weeks before transplanting were more effective than superphosphate. In Malinao soil, rock phosphate was superior over superphosphate only with incubation at field capacity. The RAE could be used to calculate relative economic effectiveness once the price level of P from the different phosphate sources is known.

Table 5.5 Effect of variation in phosphate rate, time of fertilizer application and soil moisture status on the chemical composition of rice plants on two acid sulphate soils, one month after transplanting.

time before transplanting		3 weeks	3 weeks	1 day	3 weeks	3 weeks	1 day
water status		2/3 FC	FC	flooded	2/3 FC	FC	flooded
P source	rate ppm P	Iloilo			Malinao		
<hr/>							
		N (%)					
Carolina RP	50	3.96	3.58	3.70	3.28	3.16	2.98
	100	4.01	3.74	3.50	3.40	3.46	3.20
Lumpoon RP	50	3.83	3.55	3.84	3.62	3.44	2.94
	100	4.00	3.83	3.71	3.57	3.37	2.77
superphosphate	50			4.01			3.67
control	0			3.64			3.16
<hr/>							
		P (%)					
Carolina RP	50	0.29	0.33	0.30	0.29	0.28	0.29
	100	0.35	0.36	0.33	0.32	0.31	0.26
Lumpoon RP	50	0.41	0.42	0.39	0.32	0.35	0.29
	100	0.49	0.43	0.40	0.34	0.33	0.29
superphosphate	50			0.41			0.40
control	0			0.28			0.28
<hr/>							
		Fe (ppm)					
Carolina RP	50	175	217	227	213	333	229
	100	179	234	230	263	394	217
Lumpoon RP	50	113	112	179	306	339	249
	100	166	146	245	243	370	247
superphosphate	50			217			338
control	0			204			253
<hr/>							
		Al (ppm)					
Carolina RP	50	115	146	204	121	324	223
	100	119	149	173	140	431	243
Lumpoon RP	50	156	127	113	395	336	124
	100	114	178	225	457	349	164
superphosphate	50			147			343
control	0			166			272

Table 5.6 Effect of variation in phosphate rate, time of fertilizer application and soil moisture status on the chemical composition of straw at harvest on two acid sulphate soils.

time before transplanting		3 weeks	3 weeks	1 day	3 weeks	3 weeks	1 day
water status		2/3 FC	FC	flooded	2/3 FC	FC	flooded
P source	rate ppm P	Iloilo			Malinao		
<hr/>							
N (%)							
Carolina RP	50	0.85	0.96	0.84	0.64	1.03	0.62
	100	0.98	0.98	0.87	0.63	1.16	0.75
Lumpoon RP	50	0.98	1.01	1.03	0.62	0.90	0.81
	100	0.93	1.10	1.05	0.61	0.92	0.83
superphosphate	50			1.05			0.98
control	0			0.95			0.96
<hr/>							
P (%)							
Carolina RP	50	0.08	0.10	0.08	0.06	0.10	0.06
	100	0.09	0.12	0.08	0.07	0.09	0.06
Lumpoon RP	50	0.10	0.10	0.10	0.07	0.09	0.07
	100	0.10	0.12	0.10	0.07	0.10	0.10
superphosphate	50			0.10			0.10
control	0			0.09			0.07
<hr/>							
Fe (ppm)							
Carolina RP	50	344	358	243	428	548	427
	100	361	368	273	490	561	556
Lumpoon RP	50	321	354	331	358	600	465
	100	341	460	327	377	699	614
superphosphate	50			338			415
control	0			332			516
<hr/>							
Al (ppm)							
Carolina RP	50	58	73	75	68	65	57
	100	85	83	87	69	72	81
Lumpoon RP	50	60	71	85	64	99	71
	100	92	86	82	67	110	90
superphosphate	50			79			95
control	0			96			103

Table 5.7 Relative agronomic effectiveness¹ of rock phosphate fertilizers applied at different times and rates on soils with different water status, compared with a standard superphosphate application.

time before transplanting		3 weeks			3 weeks			1 day
water status		2/3 FC	FC	flooded	2/3 FC	FC	flooded	
P source	rate ppm P	Iloilo			Malinao			
Carolina RP	50	160	104	101	16	90	4	
	100	161	108	163	26	136	16	
Lumpoon RP	50	137	76	< 0	21	122	19	
	100	204	82	104	13	124	10	

¹ Relative agronomic effectiveness:

$$RAE = \frac{\text{Yield with rock phosphate treatment} - \text{control yield}}{\text{Yield with 50 ppm P as superphosphate} - \text{control yield}} \times 100$$

Values are means of triplicates.

5.5 Conclusions and recommendations

Based on the above findings, the following conclusions can be drawn.

- 1) Olsen P values in Iloilo soil increased after leaching excess salt. Therefore, the Olsen P value for the non-leached, dry, saline soil was a poor indicator for P availability.
- 2) Rice showed little response as the application rate of rock phosphate application increased from 50 to 100 ppm P.
- 3) Rice response to different phosphate fertilization methods varied from soil to soil. Malinao soil produced the highest yield when rock phosphate was applied 3 weeks before transplanting with incubation at field capacity. Control yields on Iloilo soil were higher, but maximum yields much lower than on Malinao soil.
- 4) The relative agronomic effectiveness of phosphate indicated that rock phosphate was most beneficial in Iloilo soil with incubation at 60-70% FC for three weeks before transplanting and in Malinao soil with incubation at FC.

These findings indicate that rock phosphate, properly incubated, could

be more efficient than superphosphate on acid sulphate soils. Field experiments are needed to confirm or modify the following recommendations.

Incubation after rock phosphate application is quite feasible under field conditions. Rock phosphate can be applied direct to the ploughed field after harvesting a previous crop. These methods of rock phosphate application followed by incubation could increase rice yields in P-deficient acid sulphate soils and at the same time save the costs of manufacturing water soluble phosphate fertilizers.

Questions remaining

The low maximum grain yields on Iloilo soil compared with Malinao are not due to P-deficiency, since Olsen P values were higher than in Malinao, and since P concentrations in plants at 6 weeks age as well as in straw at harvest were similar on both soils and well above the deficiency range.

The main difference observed between the two soils was the increase in pH of the soil solution upon flooding. In Malinao, the pH rose to above 5 within 6 weeks, in Iloilo, the pH remained around 4-4.5. This would suggest that acid, toxic compounds were not reduced at a sufficiently fast rate in the Iloilo soil. Their identity is not known; however, methods to increase the rate of pH rise after inundation would probably be beneficial on Iloilo soil. Applications of manure or lime, even in small doses, would create locally favourable conditions for microbial activity and would presumably speed up the rise in pH.

Especially in Malinao, there are some indications for a positive relation between grain yield in the fertilized treatments and Fe and Al concentrations in plants one month after transplanting as well as in straw at harvest. This is contrary to expectations at the start of the experiment. The high Al concentrations are about 300 to 400 ppm, above the 300-ppm toxicity limit suggested by Tanaka and Navasero (1966), while grain yields from the same treatments are among the highest in the experiment. The lower maximum yields on Iloilo soil are not associated with particularly high Al or Fe concentrations in the plants.

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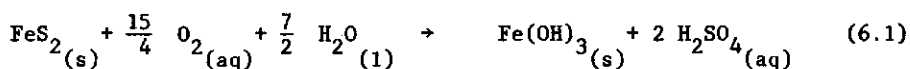
6 SIMULATION OF OXIDATION AND ACIDIFICATION PROCESSES IN ACID
 SULPHATE SOILS

Abstract

Simulation models are useful to predict the effect of one or more of the complex climatic, soil, water or chemical changes on the soil system. Such predictions can be used to make economic evaluation of, for example, the cost and benefit of reclamation work on acid sulphate soils. The objective of this study was to develop a simulation model to calculate the time course of acidity production from pyrite oxidation in relation to the changes of ground water table, evaporation, entrance of oxygen and different chemical reactions. The model is based on a multicompartment model in which the soil profile is divided into a number of layers, is written in CSMP and contains three main parts: INITITAL, DYNAMIC and TERMINAL. For each compartment of a clay loam and a silty clay soil, the compartment thickness, its water content, pyrite content, cation exchange capacity, total cations, adsorbed cations and oxygen concentrations are given as inputs. Three evaporative demands of 4, 6 and 9 mm.d⁻¹ were used as a boundary condition at the soil surface. These substantial differences in evaporative demands lead to increasing water loss. Results show that the oxidation process and the associated acidification of the soil are only marginally affected by the different evaporative demands, although the oxidation rate was very much influenced during the early part of the evaporation process.

6.1 Introduction

Acid sulphate soils are derived from marine and estuarine sediments containing high concentrations of reduced sulphur components, which upon drainage and aeration, show oxidation of sulphides (mainly pyrite, FeS_2), which leads to a definite and severe acidification due to the formation of sulphuric acid. Pyrite oxidation is a complicated process which includes several types of oxidation-reduction reactions, hydrolysis and complex-ion formation, solubility controls and kinetic effects. The overall process describing pyrite oxidation is commonly given by the following reaction:



in which pyrite and water, in the presence of oxygen, form insoluble ferric hydroxide and sulphuric acid. The quantity of acid products depends on the rate of oxidation, which is controlled by climatological and hydrological factors and soil properties. Many laboratory experiments have been carried out to determine the rate of oxidation, the acidification process, but models on pedogenesis have not received much attention and have not been the object of research on acid sulphate soils.

The composition of the soil solution as it moves through the soil, depends on its pH, the anion content and the exchangeable base composition of the soil and reflects changes in the soil system. This composition, in turn, influences the effectiveness of the soil solution as weathering agent. A model for predicting the rate of sulphate production and the degree of acidity development and oxidation under different and varying environmental conditions could be of importance for the study of improvement of acid sulphate soils. The purpose of this study is to develop and evaluate a computer simulation model for the oxidation and acidification processes in acid sulphate soils. The model is based on the moisture flow equation, calculated hydraulic conductivity and suction functions, oxygen flow and cation exchange processes in the soil. The water movement, oxygen movement and chemical processes sections are discussed separately before the presentation of the complete model.

6.2 Oxidation process in acid sulphate soils

Investigations on pyrite oxidation usually focus on two main processes: inorganic and microbiological oxidation processes. The microbiological oxidation processes involve two main species of microbes: *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans*. *Thiobacillus ferrooxidans* was identified in acid mine waters (Leathen and Madison, 1949) and later found to be capable of reducing ferrous iron under very acid conditions. *Thiobacillus ferrooxidans* oxidizes ferrous iron, pyrite and sulphur, whereas *Thiobacillus thiooxidans* oxidizes only sulphur and pyrite. The inorganic oxidation process takes place in the presence of water and oxygen. The pathways of pyrite oxidation are shown in Fig. 6.1.

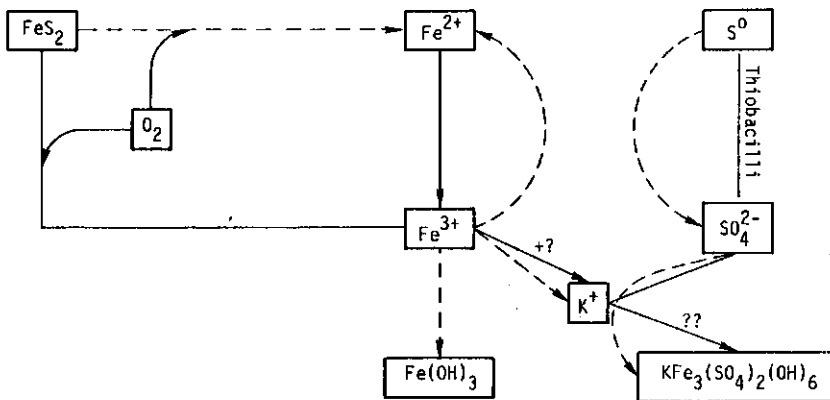
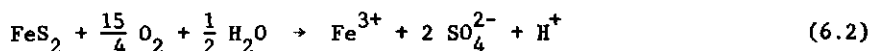


Fig. 6.1 The pathways of pyrite oxidation

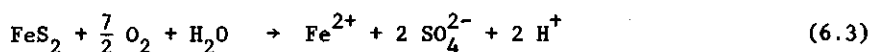
----- inorganic processes
 ————— microbial processes

In this chapter the main emphasis will be on the inorganic oxidation process. The amount of acid produced during the oxidation process depends on the initial concentrations of the reaction products and on the fate of iron sulphide. Four possible situations have been identified:

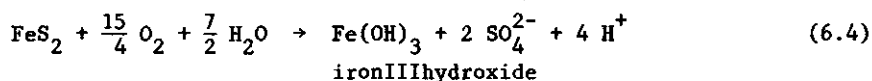
1. All iron is oxidized and remains in solution as Fe^{3+} :



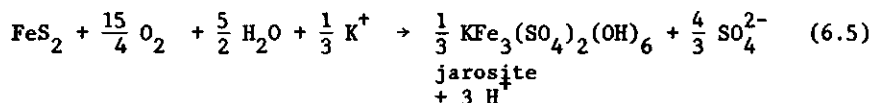
2. Iron is released as Fe^{2+} :



3. All iron is oxidized and hydrolyzed to iron (ferric) hydroxide:



4. Formation of jarosite:



The conspicuous deposition of hydrated ferric iron oxide and jarosite in young acid sulphate soils suggests that the net result of pyrite oxidation in sulphuric materials is represented by equations (6.4) and (6.5).

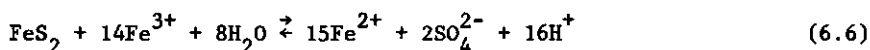
The ferrous iron, hydrogen and sulphate ions released during pyrite oxidation normally undergo various further reactions in the soil. Essentially all ferrous iron is oxidized to ferric iron, which either precipitates as ferric hydroxide, $\text{Fe}(\text{OH})_3$, or jarosite, $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$. The larger part of the sulphate released during pyrite oxidation remains in solution and is removed from the soil by leaching, and by diffusion into the surface water if present. The remaining sulphate partly precipitates, either as jarosite or as basic aluminium sulphate,

$\text{Al}(\text{OH})\text{SO}_4$ (van Breemen, 1973) and is partly adsorbed, mainly by ferric oxides. Under different weather and soil conditions, different products of sulphate can be formed such as gypsum, $[\text{CaSO}_4 \cdot 2\text{H}_2\text{O}]$, sodium alum, $[\text{NaAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}]$, etc. Sulphate can be reduced again to sulphides, which may temporarily be fixed as FeS in reduced conditions.

Many factors influence the rate of pyrite oxidation. Its rate-limiting step in the soil is the supply of oxygen (van Breemen, 1973). The effect of oxygen concentration on oxidation rate is quantified differently among investigators. Using stability diagrams, van Breemen (1973) concluded that O_2 and Fe^{3+} are the only two oxidants active in pyrite oxidation under natural conditions. Some investigations (Hart, 1962; van Breemen, 1973) indicated that the initial products of pyrite oxidation are elemental S and Fe^{2+} , while others (Garrels and Thompson, 1960; Silverman, 1967; Bloomfield, 1972) reported that SO_4^{2-} is released almost instantaneously during pyrite oxidation to Fe^{3+} . Elemental S is formed at higher pH values in this oxidation pathway.

Van Breemen (1976) argues that in acid ($\text{pH} < 4.4$) oxidized environments ($\text{Eh} > 400 \text{ mV}$) jarosite is more stable than amorphous ferric oxide and field observations confirm that the more severe the acidity, the more dominant is jarosite deposition over iron oxide deposition.

Direct oxidation of pyrite by ferric iron with production of acidity has been reported and is represented by the following equation (Singer and Stumm, 1970):



When pH decreases to values below 4.5, ferric iron becomes more soluble and begins to act as an oxidizing agent and below a pH of 3.0 it is the only important oxidizer of pyrite. The presence or absence of oxygen does not influence the oxidation rate by ferric iron (Singer and Stumm, 1970).

Other factors affecting the inorganic oxidation rate include temperature, surface area of pyrite, the presence of impurities such as trace metals and the presence of other minerals such as chalcopyrite, sphalerite, calcite, etc.

Sveshnikov and Dobychin (1956) pointed out that rates of metal release

from different sulphides are related to their electrode potentials and that a mixture of sulphides releases more metals into solution and decreases the pH more than mono-mineralic samples. The presence of relatively inert conductors such as graphite has also been proposed to enhance the oxidation rate by increasing the electron flow between the anodic and cathodic portions of an ore body (Cameron, 1979). Temperature causes the oxidation rate by oxygen to double for every 10°C rise (Shumate et al., 1971).

These additional factors may or may not be important, depending on the particular geological and weather conditions to which the oxidizing pyrite is exposed. The surface area effects seem to be very important in the initial stages of acid sulphate production, but as the pH decreases to 3 or less it seems to be less important. Pyrite can vary significantly in grain size and morphology. Pyrite in coal deposits has been found in at least six different forms, and the most reactive form is framboidal pyrite consisting of pyrite crystals less than a micrometer in size (Caruccio et al., 1976). The occurrence of framboidal pyrite has been used to estimate the acid forming potential of coal refuse (Caruccio, 1975).

Several investigators have recognized a positive effect of smaller particle size on pyrite oxidation rate (Quispel et al., 1952; Temple and Delchamps, 1953; Hart, 1962). This effect has been attributed to lattice defects (van Breemen and Harmsen, 1975) and to increased surface area which increased reactivity (Stum and Morgan, 1970). Harmsen et al. (1954) described soils containing significant amounts of pyrite that had not acidified after drainage. They postulated that several polysulphide fractions contributed to the stability of pyrite, but gave no chemical or mineralogical evidence as support. Van Breemen (1973) suggested that preservation was due to the large particle size (between 10 and 100 μm in diameter), combined with a relatively high pH. At higher pH values, a protective coating of Fe_2O_3 may form on the pyrite surface, thus slowing the oxidation rate. Harmsen et al. (1954) and Quispel et al. (1952) reported that high levels of dissolved P strongly depressed the decomposition of pyrite at pH values above 4 due to precipitation of iron as FePO_4 .

6.3 Computer simulation of the oxidation process

In the preceding section, the effect of various factors on the rate and degree of pyrite oxidation was discussed. These factors in turn may be affected by environmental conditions such as soil type and weather. If all relevant relations can be formulated mathematically and if in addition these relations can be quantified, a model can be constructed describing the overall oxidation process in acid sulphate soils.

Computer simulation is the construction of mathematical models containing the essential features of a real system, the implementation of such models on a computer (analog, digital, or hybrid), to arrive at a solution and the study of the properties of such models in relation to those of the real system; or "the building of a model and the study of its dynamic behaviour". A model is a simplified representation of a system, a limited part of reality with well-defined boundaries. A model can be built if the structure of the system under consideration is sufficiently understood, so that the various processes playing a role in the system can be described mathematically. Simplification of the real system is axiomatic in modelling, otherwise the system itself could be used in the study; moreover, our understanding of reality is often limited.

A simulation model represents the processes, which in reality proceed continuously, in a series of discrete steps. The changes from one moment to the next one are calculated taking into account all factors that affect the system. The state of the system at any time can be defined quantitatively by the values of the state variables and changes in these states can be described mathematically.

The values of the state variables (mathematically represented by integrals), such as the amount of water, the amount of oxygen and so on, are known at any moment. The rate of change of each state variable is determined by the state of the system and the environment, so that rates are never mutually dependent. When all rates are calculated they are realized over a short time-interval to arrive at the new values of the state variables.

The simulation model is based on a multicompartment model, e.g. the soil profile is divided into a number of layers (de Wit and van Keulen,

1972). Fig. 6.2 is a schematic representation of the soil profile, divided into 20 compartments. For each compartment, the thickness of the compartment, its water content, pyrite content, cation exchange capacity, total cation content, adsorbed cations and oxygen concentration are given as input at the onset of the calculations, as is the level of the groundwater table (initialisation).

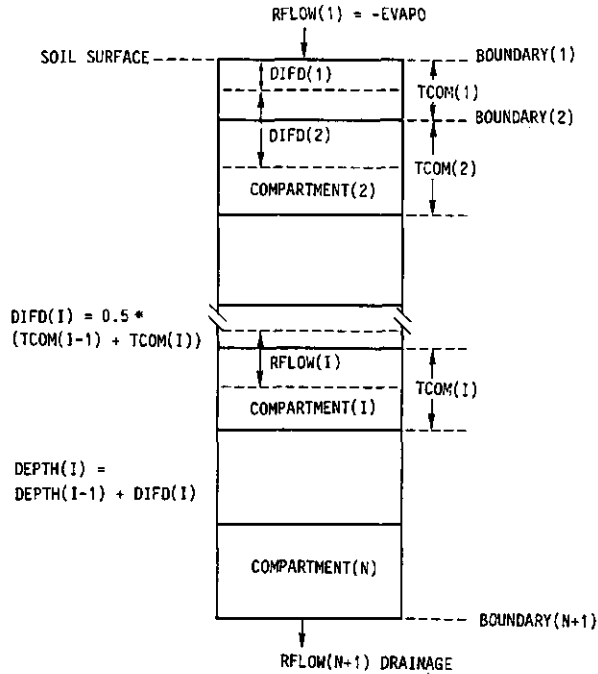


Fig. 6.2 Geometry of the system and symbols used in the program for the oxidation and acidification processes in acid sulphate soils.

All characteristics of the soil that depend on the state of the system, such as soil moisture suction and unsaturated conductivity for each compartment, are derived in the model during the simulation from the soil-specific functions relating these variables to moisture content. Potential evaporation and rainfall are introduced as forcing functions, that are not influenced by the behaviour of the system.

During the simulation, changes in soil moisture content and chemical changes are calculated for each layer based on water balance and chemical equilibria, respectively. Changes in groundwater table depth, following evaporation or rain are taken into account. The geometry of the system and symbols used in the program for the oxidation and acidification processes is represented in Fig. 6.2.

The program is written in CSMP (IBM, 1972) and contains three main parts: INITIAL, DYNAMIC and TERMINAL.

All operations specified in the INITIAL part of the program are carried out once prior to the actual simulation. All operations defined in the DYNAMIC part are performed repeatedly for each elapsed time-interval during the period of simulation. Integration is carried out by standard system routines in CSMP. Finally, in the TERMINAL part calculations are performed which are to be made only after the dynamic section has been completed.

6.4 Water movement section

Water in the soil moves from points with a high potential (energy status) to points with a lower potential. The total potential consists of the matrix potential ψ_m , also known as the capillary potential, the gravity potential ψ_g and the osmotic potential, ψ_{osm} :

$$\psi = \psi_m + \psi_g + \psi_o \quad (6.7)$$

The potential is expressed as energy per unit mass of water, i.e. J/kg, or as energy per unit volume of water, i.e. J/m³ or Pa. In hydrology, hydraulic head (in m or cm water) is still often used. This quantity is equivalent to 98.1 Pa (approximately 0.1 J.kg⁻¹) at the earth's surface. In the following, we will express potential in terms of hydraulic head.

At the level of the groundwater table the matrix potential is zero. The matrix potential is negative in unsaturated soil, i.e. above the groundwater. The gravity potential is defined as the distance to a reference level for which the groundwater table is chosen. Defining z as

The average conductivity is calculated as the arithmetic average of the conductivities of the two compartments (de Wit and van Keulen, 1972):

$$KAV(N) = (K(N-1) + K(N))/2$$

The hydraulic conductivity of each compartment is obtained from an experimentally determined relation between conductivity and the volumetric water content of the compartment with:

$$K(N) = AFGEN (KTBN, WC(N))$$

The AFGEN statement provides linear interpolation in a given tabulated function, entered in the program in the following form:

FUNCTION KTBN = (0.05, 1.E-10), (0.10, 1.E-5), (0.15, 5.3E-3), ...

This function presents the relation between the dependent variable, the conductivity, the last number of each pair and the independent variable, the volumetric water content, the first number of each pair. By introducing different relations for different compartments it is possible to introduce a layered soil. The actual interpolation is then most conveniently executed by the use of a TWOVAR function, which enables the simultaneous use of water content and depth as independent variables.

In the same way the matric suction of the compartment (SUCT(N), in m H₂O) is obtained from tabulated functions, which again may differ for different compartments, with:

$$SUCT(N) = AFGEN (SUCTT, WC(N))$$

If a hydraulic head is present, the water in the soil may be above atmospheric pressure, but the relation between volumetric water content of the soil and its matric suction is generally only given in the region below atmospheric pressure. The compressibility of water is so low, that for a completely saturated soil the potential would increase practically at an infinite rate with increasing water content. In prac-

tice, always some air is enclosed and compressed according to Boyle's law. Hence, the suction curve may be extended in the region above atmospheric pressure with a finite slope.

To arrive at the hydraulic potential (in $\text{m H}_2\text{O}$), the gravity potential must be added to the matrix suction. Thus:

$$P(N) = \text{SUCT}(N) + \text{GRP}(N)$$

The gravity potential is calculated with respect to the depth of the groundwater table as:

$$\text{GRP}(N) = \text{DPGWT} - \text{DEPTH}(N)$$

where,

DPGWT = depth of the groundwater table in m

$\text{DEPTH}(N)$ = the distance from the middle of the compartment to the soil surface in m.

The flow rates over the first and the last boundary are defined differently, according to pre-defined boundary conditions. These may be any time-dependent potential or flow rate.

The flow rate into the first compartment (FLOW1 in $\text{m}^3 \text{m}^{-2} \text{d}^{-1}$) equals the rate of soil surface evaporation, EVAPO .

This rate is derived from the potential evaporation rate, calculated from the equation developed by Jackson, 1973 and Jackson et al., 1973 as follows.

$$\text{PET} = \text{AMAX1} (0.0, \text{AMP} * \text{SIN} (2.* \text{PI} * \text{TIME}/86400))$$

where,

$\text{AMP} = \pi$ times the average evaporativity AVPET , is defined as a fixed value in the initial section.

The AMAX1 function takes the maximum value of the two arguments; its use in this statement prevents the potential evaporation rate from

becoming negative and sets the nighttime evaporation rate at zero. In principle, the night-time evaporation rate can be set at any other finite value or fraction of AVPET. Steady evaporativity such as may be set in controlled conditions, can simply be simulated with the alternative statement:

PET = AVPET

The actual evaporation rate is set equal to the potential rate as long as the matrix potential of the top compartment remains higher than the initially specified air - dryness value, MINPOT:

IF (MPOT(1) . GT . MINPOT) EVAP = PET

After the top compartment has dried out to its minimum (air-dry) matric potential, it can not loose any more water and the evaporation rate becomes equal to the rate of transmission of moisture from the profile (or to the potential rate, whichever is smaller):

IF (MPOT(1) . LE . MINPOT) EVAP = AMIN1 (PET, - RFLOW(2))

In either case,

RFLOW(1) = -EVAP

where,

RFLOW(1) = the flux of water through the soil surface.

The movement of the groundwater table resulting from changes in the water content in the profile is based on the following assumptions (Belmans et al., 1983):

If the groundwater level is set at a fixed value (controlled conditions), a pressure head boundary condition at the bottom of the unsaturated zone is used which is most conveniently placed at the bottom of a compartment. In the case of a fluctuating groundwater level, the size of the compartment situated just above the groundwater may vary

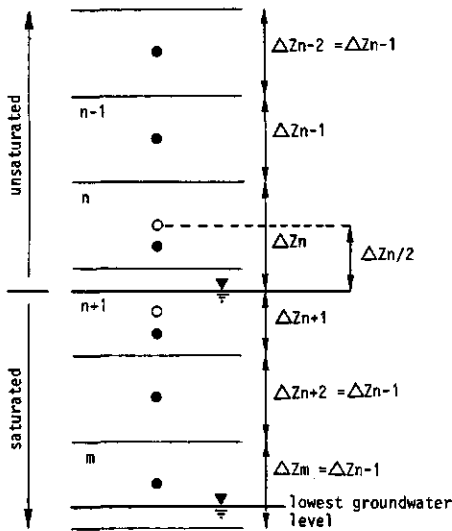


Fig. 6.3 Illustration of the varying size (ΔZ_n) of the first unsaturated soil compartment situated just above the groundwater level.

(Fig. 6.3). It is equal to the distance between the groundwater level and the bottom of the overlying compartment (ΔZ_n). The pressure head h in the center of the compartment of flexible thickness n is at any moment considered to be in equilibrium with the groundwater level, i.e. $h_n = \Delta Z_n/2$. Also the nodal point just below the groundwater table changes in position. This equilibrium procedure is followed to avoid instability in computation, assuming that the equilibrium situation close to the groundwater level does not deviate much from the real situation. At each time step the water contents of all compartments in the unsaturated zone are updated according to the equations given above, except that of compartment $n-1$, which is maintained in equilibrium with the groundwater level. Then the thickness and pressure head of compartment $n-1$ are adjusted to the new groundwater level (equilibrium again). The change in groundwater level is considered to occur as a consequence of the transfer of water from the saturated to the unsaturated zone (negative or positive).

The water balance of the soil profile can be written for each time step as:

$$\text{DELW} = \sum_{i=1}^n \text{NFLW}(I) \times \text{DELT}$$

where,

DELW = change in water storage in the total soil profile.

If DELW is positive in the model, water has moved from the saturated to the unsaturated zone in the soil profile which entails lowering of the groundwater level. On the other hand, if DELW is negative there is a rise in groundwater level.

On the basis of the value of DELW, at the end of each time step, a new adapted groundwater level is calculated according to the following procedure: If the absolute value of DELW exceeds 10^{-5} , then:

1. The groundwater level is lowered by a depth DELW.
2. The number of unsaturated compartments, n-1 determined.
3. The thickness Δz_n and equilibrium pressure head h_n of compartment n are calculated.
4. The pressure-head profile of the first four nodal points, i.e. the first four compartments above the groundwater level is smoothed by a redistribution procedure, taking as boundary conditions at the top a flux equal to zero and at the center of compartment n, $h = h_n$. The "time" step used in this procedure is not real, i.e. simulation time remains unchanged.
5. The change in water storage over the entire system is computed and added to DELW, whose absolute value decreases.
6. If the absolute value of DELW $< 10^{-6}$ the procedure stops; otherwise steps (1) to (5) are repeated.

6.5 Flow of oxygen in the soil profile

Oxygen movement in soils is mainly governed by two processes: mass flow and diffusion flow. Mass flow is due to the difference in total gas-pressure. In wet soils, for example, many air-filled pores are discon-

tinuous or blocked by water films and oxygen diffusion is slow. In those cases, differences in total pressure may be sufficient to break these films and cause some mass flow. Another form of mass flow is the transfer of dissolved gases by rain or irrigation water percolating into or through the soil. Water at 25°C, in equilibrium with air at atmospheric pressure contains about 6 ml. O₂ per liter.

Diffusion is the transfer of gaseous molecules through porous media and liquids at the same temperature and pressure under the influence of a concentration gradient. The diffusion in one direction can be described as:

$$F \cdot A = \frac{dq}{dt} = - D \frac{dc}{dx} \cdot A \quad (6.11)$$

where,

F = rate of transfer per unit area of section (g.cm⁻².s⁻¹)

A = area (cm²)

q = amount of gas (g)

t = time (sec)

c = concentration (g.cm⁻³)

x = distance along the line of flow (cm)

D = diffusion coefficient (cm².s⁻²).

The diffusion coefficient in soil is commonly given as the ratio D/Do, where D is the diffusion coefficient in soil (cm² s⁻¹) and Do is the diffusion coefficient of the same gas in air at the same temperature and pressure. The ratio D/Do depends on soil properties only, notably its pore geometry and not on the gas used for diffusion measurements (Penman, 1940a; 1940b).

For a short range of E_g the relation between D/Do and gas-filled pore space E_g (cm³ air.cm⁻³ soil) can be described by (Penman, 1940a; 1940b):

$$D/Do = 0.66 E_g \quad (6.12)$$

Similar results were obtained by van Bavel (1952b) and Flegg (1953). For a wider range of porosities, the following relationship is reported

by Currie (1960a,b):

$$D/D_0 = \gamma E_g^\mu \quad (6.13)$$

where,

γ and μ are coefficients determined from regression analysis.

Work on the ratio D/D_0 from different sources was reviewed by Bakker and Hidding (1970). The relationship between D/D_0 and E_g used in our model was based on the work of Leffelaar (1977).

The ratio D/D_0 for each soil compartment is obtained from a function based on tabulated values of Fig. 6.4.

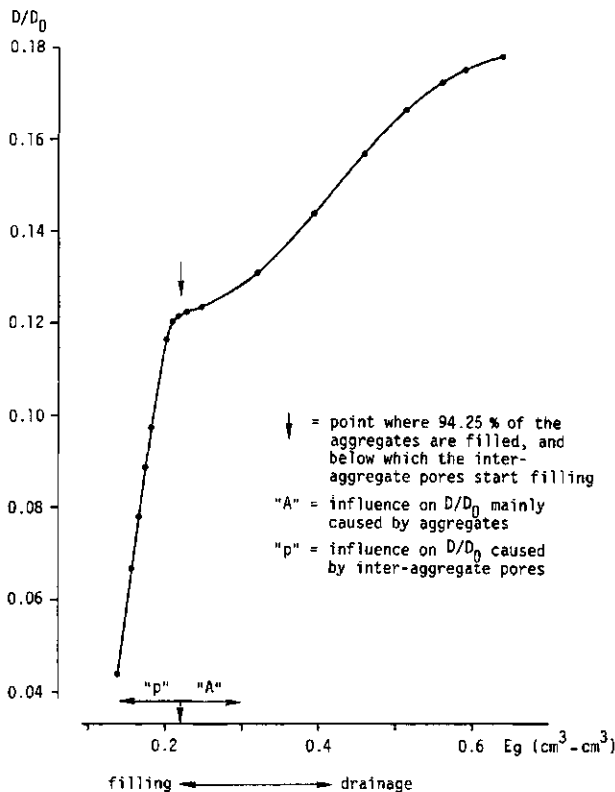


Fig. 6.4 The relation between D/D_0 and gas-filled porosity, E_g in an aggregated soil (Leffelaar, 1977).

$$\text{DEFAC}(I) = \text{AFGEN}(\text{DEFACT}, \text{PVOL} - \text{WC}(I))$$

where,

DEFAC = the diffusion efficiency factor.

The effective diffusion coefficient, DEF, is subsequently calculated by:

$$\text{DEF}(I) = \text{DZERO} \times \text{DEFAC}(I)$$

where,

DZERO denotes D_o , the diffusion coefficient of oxygen in free air.

The average diffusion coefficient for flow between two adjacent compartments is calculated as:

$$\text{ADEF}(I) = (\text{DEF}(I) + \text{DEF}(I-1))/2$$

and the rate of oxygen diffusion is calculated similar to the rate of water flow, from the diffusion coefficient and the gradient of oxygen concentration in the two adjacent layers:

$$\text{DFLOX}(I) = \text{ADEF}(I) \times (\text{COX}(I-1) - \text{COX}(I)) / (0.5 \times (\text{TCOM}(I-1) + \text{TCOM}(I)))$$

The flow rates of oxygen over the first and the last boundary again must be calculated in a different way. The flow rate into the first layer, DFLOX(1), is greatly dependent on whether or not a water layer is present on the soil surface. It is defined as:

$$\text{DFLOX}(1) = \text{FCNSW}(\text{THWL}, \text{FLO}, \text{FLO}, \text{RDFLO})$$

FLO and RDFLO are defined by:

$$\text{FLO} = \text{DEF}(1) \times (\text{COUT} - \text{COX}(1)) / (0.5 \times \text{TCOM}(1)) \quad \text{if } \text{THWL} = 0$$

$$\text{RDFLO} = \text{DZW} \times (\text{COUT} - \text{COX}(1)) / (\text{THWL} + \text{NOT}(\text{THWL})) \quad \text{if } \text{THWL} > 0$$

where,

COUT = the concentration of oxygen in the atmosphere

DZW = the diffusion coefficient of oxygen in water

THWL = the thickness of a water layer on top of the soil

NOT = a function that assumes the value 1 if the argument is smaller or equal to zero and is otherwise zero. It is used to prevent by zero division when no water layer is present.

Diffusion of oxygen into the soil profile is seriously impaired by the presence of a water layer as the diffusion coefficient of oxygen in water is about 10^4 times smaller than that in air. The rate of diffusion of oxygen over the groundwater boundary is set to zero.

Mass flow of oxygen due to changes in soil moisture content in the profile is calculated under the assumption that air moves in or out of each compartment fully complementary with the water:

$$MFLOX(I) = NFLW(I) \times COX(I)$$

Net flow of oxygen is finally calculated from the flow rates over the upper and lower boundaries of a compartment, and the oxygen consumption rate in that compartment.

$$NFLOX(I) = DFLOX(I) - DFLOX(I+1) - MFLOX(I) - RCOX(I)$$

RCOX is the consumption rate of O_2 which is discussed in section 6.5.6.

6.5.1 The diffusion coefficient of oxygen in an aggregate, DCSPH

Lemon and Wiegand (1962) give the diffusion coefficient for oxygen in free water as $2.6 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ at 25°C . The ratio of the diffusion coefficient in a porous medium to that in a medium without any solid obstacle, D/D_o , equals 0.0566 for a porosity of 0.465 (Leffelaar, 1977).

Combining both values and converting to days, yields the diffusion

coefficient of oxygen in a water saturated aggregate:

$$D = 0.0566 \times 2.6 \times 10^{-5} \times 86400 = 1.2715 \times 10^{-1} \text{ cm}^2 \cdot \text{d}^{-1} \\ = 1.2715 \times 10^{-5} \text{ m}^2 \cdot \text{d}^{-1}$$

6.5.2 The relative solubility of oxygen in water, S_{OL}O

Grabbie (1966) reports a value of $0.039 \text{ g O}_2 \text{ l}^{-1}$ water at 25°C and 1 bar pressure. Assuming 21% of oxygen in air, it follows that the concentration equals $0.21 \times 1.3089 \times 10^{-3} = 2.7487 \times 10^{-4} \text{ g O}_2 \text{ cm}^{-3}$ of air. The relative solubility follows from the ratio of the amount of oxygen in water to that in air and amounts to $0.039 \times 10^{-3} / 1.3089 \times 10^{-3} = 2.9796 \times 10^{-2}$.

6.5.3 The critical concentration of oxygen, C_{CO}

Greenwood (1961) reported respiration to be inhibited at an oxygen concentration of about 7×10^{-7} molar. Conversion of this value to $\text{g O}_2 \text{ cm}^{-3}$ of soil yields $7 \times 10^{-7} \times 32 \times 10^{-3} = 2.24 \times 10^{-8}$, a number that was used by van Veen (1977).

6.5.4 Diffusion coefficient of oxygen in free air, D_{ZERO}

Grabbie (1966), reported a value of $0.226 \text{ cm}^2 \cdot \text{s}^{-1}$ at 25°C, equivalent to $19626.4 \text{ cm}^2 \cdot \text{d}^{-1}$. The oxygen concentration in free air, C_{OV}T, and the diffusion coefficient in free water are given above, and are known therefore.

6.5.5 The ratio D/D_o for soil/air

The ratio D/D_o gives the diffusion coefficient of molecules in a porous system (D) compared to the diffusion coefficient in the same medium

(water or air) without any solid obstacle. Analytical solutions for the description of soil aeration under uniform conditions have been given by van Bavel (1951, 1952a) and Taylor (1949). Soil structure inevitably causes heterogeneity in soils, a factor investigated by Bakker and Hidding (1970) and Currie (1960a, 1960b, 1961a, 1961b). Currie presented detailed results with respect to diffusion in systems having clear distinction between intra- and inter-aggregate pores, and carried out measurements in both dry and wet materials.

In the present study the ratio D/D_0 is based on the calculation proposed by Leffelaar (1977).

6.5.6 Oxygen consumption, $RCOX$

Oxygen is consumed by root respiration if plants are present, by microbial respiration and by pyrite oxidation. Grable (1966) reported values for oxygen consumption ranging from 5 to 10 $l.m^{-2}.d^{-1}$. Bakker and Hidding (1970) reported the highest value of Grable for only microorganisms ($\pm 8.9 l.O_2.m^{-2}.25\text{ cm depth}^{-1}.d^{-1}$). Furthermore, Woldendorp (1963), showed that ratio of respiratory activity roots to microorganisms was about 2 to 1. This would imply that the highest reasonable estimate of oxygen consumption may be about $26.67 l.O_2.m^{-2}.25\text{ cm depth}^{-1}.d^{-1}$.

The model assumes that 40 percent of the oxygen entering the pyritic layers is consumed by pyrite oxidation.

6.5.7 The sulphate production, (PSO_4) and the acid production, $RHYD$

The sulphate production depends on the amount of oxygen and is calculated from equation (6.2). The amount of sulphate is equal to $\frac{192}{120} g O_2 = 1.6 g O_2$ and the acid production is equal to $\frac{2}{96} g SO_4 = 0.0208 g SO_4$.

6.6 Transport of cations in the soil profile

In this section the cation exchange processes and the movement of different cations is treated. In most soils, a considerable amount of immobile negative charges is present. These charges are associated with the presence of clay particles and organic matter particles. In the case of the clay particles these negative charges are the result of processes that occurred during the formation of their lattice, consisting of SiO_4 and $\text{AlO}_4(\text{OH})_x$ configurations. In part of the lattice the Si and/or Al ions have been replaced by cations of lower valence because the Al- and Si-atoms were not present in the required ratio. A direct consequence of this substitution is a deficit of positive charge in the lattice.

Because electroneutrality must be maintained, these deficits in the lattice are compensated by the absorption of positive ions on the surface of the lattice. These ions, however, may be exchanged with other positive ions in the soil solution. This exchange process is very rapid, so that it may be assumed in general that at any moment equilibrium exists between the concentration of the various positive ions in the soil solution and those adsorbed on the soil matrix.

Because the composition of the soil solution may change as a result of the processes associated with the oxidation of pyrite, and transport due to mass flow and diffusion, a quantitative description of the exchange process is necessary.

The total negative charge of the soil matrix is termed the CEC, or cation exchange capacity, and is commonly expressed in meq. per 100 grams of dry soil material. Its value is determined by the combined effect of the charge per unit of area (surface density of charge in keq m^{-2}) which is a function of clay type and the area per unit of weight (specific surface area in $\text{m}^2 \text{ kg}^{-1}$) which is a function of clay type and main constituent ion.

In this chapter the cations H^+ , Ca^{2+} , Al^{3+} , K^+ , Na^+ , Mg^{2+} are included in the model, instead of only the few cation exchange reactions that have traditionally been considered in simulation studies of salt transport.

6.7 Calculation of the composition of the exchange complex and the soil solution for five cations

To calculate the distribution of ions between the solution and the adsorption complex, the equilibria between the cations in solution and the exchangeable cations for the various combinations is defined as:

$$\frac{K_{\text{sol}}}{Na_{\text{sol}}} = Y_1 \frac{K_{\text{ads}}}{Na_{\text{ads}}} \quad (6.13)$$

$$\frac{Mg_{\text{sol}}}{Ca_{\text{sol}}} = Y_2 \frac{Mg_{\text{ads}}}{Ca_{\text{ads}}} \quad (6.14)$$

$$\frac{Ca_{\text{sol}}}{(Na_{\text{sol}})^2} = Y_3 \frac{Ca_{\text{ads}}}{(Na_{\text{ads}})^2} \quad (6.15)$$

$$\frac{H_{\text{sol}}}{Na_{\text{sol}}} = Y_4 \frac{H_{\text{ads}}}{Na_{\text{ads}}} \quad (6.16)$$

$$\frac{Al_{\text{sol}}}{(Na_{\text{sol}})^3} = Y_5 \frac{Al_{\text{ads}}}{(Na_{\text{ads}})^3} \quad (6.17)$$

The subscripts sol and ads refer to the dissolved and adsorbed fractions, respectively.

Y_1 , Y_2 , Y_3 , Y_4 and Y_5 are the exchange constants for the respective cation pairs which are introduced in the model as fixed values; they include the activity coefficients of the ions in solution.

All concentrations are expressed in eq/m^3 .

The sum of the concentrations of the six adsorbed cations must be equal to the cation exchange capacity in each layer according to:

$$H_{\text{ads}} + Na_{\text{ads}} + K_{\text{ads}} + Ca_{\text{ads}} + Mg_{\text{ads}} + Al_{\text{ads}} = \text{CEC} \quad (6.18)$$

In the model, the CEC is a variable which is a function of depth only and is independent of pH and complex composition. If K_{tot} , Ca_{tot} , Na_{tot} , Mg_{tot} , H_{tot} and Al_{tot} are used for the total amounts of the various cations (solid + liquid phase) and $X_1 = Na_{sol}/Na_{ads}$, then equations (6.13) to (6.15) can, after rearrangement, be substituted in equation (6.18):

$$CEC = \frac{Na_{tot}}{1+Y_1} + \frac{K_{tot}}{1+X_1Y_1} + \frac{H_{tot}}{1+X_1Y_4} + \frac{Ca_{tot}}{1+X_1^2Y_3} + \frac{Mg_{tot}}{1+X_1^2Y_2Y_3} + \frac{Al_{tot}}{1+Y_1^3Y_5} \quad (6.19)$$

As the rate of exchange is high compared with the rates of diffusion, dispersion and water flow, Eqn. (6.19) is used to calculate for any compartment the distribution between adsorbed ions and ions in solution.

X_1 is found from Eqn. (6.19) by a method of successive better approximations using the Newton-Raphson method as elaborated in the IBM-SSP subroutine RTNI, modified to facilitate the choice of a correct initial value for the iterative procedure.

Substitution of the value of X_1 in Eqns. 6.13 through 6.17 provides the values for Na_{sol} , K_{sol} , Ca_{sol} , H_{sol} , Mg_{sol} , Al_{sol} , Na_{ads} , K_{ads} , Ca_{ads} , H_{ads} , Mg_{ads} and Al_{ads} .

The use of subroutine RTNI is explained in detail in the IBM Programmers' Manual (1968). Only some salient points are highlighted here. The subroutine refines the initial guess XST of a root of the general non-linear equation $f(x) = 0$ according to Newton's iteration scheme:

$$x_{i+1} = x_i - \frac{f(x_i)}{f'(x_i)} \quad (i = 0, 1, 2, \dots)$$

Each iteration step requires one evaluation of $f(x)$ and one evaluation of $f'(x)$. Both $f(x)$ and $f'(x)$ are calculated in an externally added subroutine CAT, where $f(x)$ is defined by FF:

$$\begin{aligned}
 FF = CEC - \frac{Na_{tot}}{1+Y_1} + \frac{K_{tot}}{1+X_1Y_1} + \frac{H_{tot}}{1+X_1Y_4} + \frac{Ca_{tot}}{1+X_1^2Y_3} + \frac{Mg_{tot}}{1+X_1^2Y_2Y_3} \\
 + \frac{Al_{tot}}{1+X_1^3Y_5}
 \end{aligned} \tag{6.20}$$

$f'(x)$ is the first derivative of FF with respect to x and is defined as DERF in the model.

The expression for DERF is rather long, therefore the reader is referred to the listing of subroutine CAT. Within subroutine RTNI, subroutine CAT is called by the dummy name FCT. In the original version of RTNI, the iteration procedure is terminated if a prespecified error criterion, controlled by EPS, is satisfied. If after a preset number of iterations the error criterion is not satisfied, the iteration ends with an error return (IER = 1).

If the error criterion is not satisfied within the number of iterations permitted, a new round of iterations was started, allowing for less accurate results. This is achieved by increasing EPS by a factor of 10; if necessary, this can be repeated once more, resulting in a maximum increase in EPS by a factor of 100. The indicator IEPS records how many times this feature is used.

A second feature that was introduced is a correction for those situations where the adjustment factor $f(x_i)/f'(x_i)$ is greater than x_i , or in the symbols of the routine RTNI, if DX is greater than X. This may be so if the first guess of X is too far out. Then, arbitrarily, DX is reduced to $0.9 \times DX$, which is repeated until a value is reached where DX is less than X.

Usually this procedure works quite well and allows normal termination of the iteration. If the decrease in DX is still required for the last iteration step ($I = 20$), the routine does not provide a solution due to insufficient convergence. Then the iteration is terminated, and the error indicator IER is set to 4. The call of RTNI results normally in a value for z (ratio Na_{sol}/Na_{ads}) and values for the indicators IER, I, IEPS. The last three are not further used in the model, but during debugging stages they are used to trace malfunctioning of the subroutine.

6.8 Calculating cation transport in the soil profile

The basis of all calculations of transport of substances in soil is the law of conservation of mass. For one-dimensional flow with a uniform macroscopic flow velocity, the conservation equation may be written as:

$$\frac{\partial s_i}{\partial t} + \frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial x^2} - V_i \frac{\partial c_i}{\partial x} + \phi_i \quad (6.21)$$

where,

c_i = the concentration of solute i in solution expressed as mass of solute per unit volume of solution

s_i = the concentration of solute i in the soil solution associated with the adsorbed phase

D_i = the apparent diffusion coefficient of the solute

V_i = the average interstitial velocity of the solution

ϕ_i = the production term, i.e. the net rate at which the mass of solute i is produced per unit volume of solution due to a specific transformation.

In the present model the production term is calculated for acid only, based on equation (6.2).

The production of acid resulting from pyrite oxidation is calculated as:

$$R_{PHYD} (I) = PSO_4 (I) \times 0.0208$$

$$\text{and } PSO_4 (I) = RFLOX (I) \times 1.6$$

based on the assumption that the products of pyrite oxidation are mainly ferric hydroxide, $Fe(OH)_3$, and sulfuric acid, H_2SO_4 .

The rate of flow of a chemical substance from one compartment to the next one is equal to the product of the concentration in solution and the flow rate of the solution (mass flow), plus the flow rate due to diffusion and dispersion.

The mass flow of a given ion is assumed to take place from the middle of one compartment to the middle of the adjacent one. To avoid the phenomenon of mathematical dispersion, the concentration used in the calculation is obtained by averaging the concentrations of the two compartments (Goudriaan, 1973).

For each cation the concentration is calculated from the amount in each compartment with:

$$CX(I) = CXSA/WC(I)$$

where,

X stands for the acronym of each of the six relevant cations.

Mass flow over the Ith boundary (Fig. 6.2) is then for each cation represented by:

$$MFLX(I) = RFLOW(I) \times .5 \times (CX(I) + CX(I-1))$$

The transport of ions by diffusion is proportional to the concentration gradient and to the diffusion coefficient. The latter is smaller in soils than in pure water, because only part of the volume is occupied by water. Moreover, the soil pores form a labyrinth, hence the ions have to traverse a longer path than the distance between two points. The diffusion coefficient in water is therefore multiplied by the volumetric water content and a tortuosity factor. The latter is also a function of the water content, but so little is known quantitatively about this relation, that it is generally assumed to be a constant, having a value between $\sqrt{2}$ and $\sqrt{3}$. In addition to the "pure" diffusion flow there is dispersion of the solutes as a result of the velocity distribution of the solution in pores of different size. This dispersion flow is also proportional to the concentration gradient and the proportionality factor is the product of the average flow rate of the solution and a dispersion factor. The latter has a value ranging from 0.7 for coarse sands to 7 for loamy soils (Frissel et al., 1970).

To describe the diffusion flow for each of the cations, first the apparent diffusion coefficient is defined:

$$APDIFX(I) = (DNOTX \times WC(I) \times TORT + RFLOW(I) \times DISP) / DIFD(I)$$

where,

DNOTX = diffusion coefficient ($m^2.d^{-1}$)
 TORT = tortuosity factor (unitless)
 DISP = dispersion factor (m)

and subsequently the flow rate is defined by:

$$DFLH(I) = APDIFX(I) \times (CHYD(I-1) - CHYD(I))$$

The mass flow and diffusion flow of cations over the upper and lower boundary of the soil profile are assumed to be zero.

The net flow of each cation is calculated with:

$$NFLX(I) = MFLX(I) - MFLX(I+1) + DFLX(I) - DFLX(I+1)$$

Only in the case of hydrogen a slightly different formulation is used, to account for its production in the oxidation process:

$$NFLHYP(I) = MFLH(I)MFLH(I+1) \dots + RPHYD(I)$$

The integration is carried out with:

$$AX = INTGRL(TXI, NFLX, 20)$$

In the present model the rectilinear integration routine is used, with a time step of 0.001 day.

6.9 Results and discussion

It appeared impossible at this stage to obtain sufficient accurate data for calibration and validation of the model.

To test the performance of the model, therefore, some sensitivity tests were carried out. These were directed at testing the effect of differ-

ent soil types and various evaporative demands on model output relevant to the acidification process.

Two soil types were tested, a clay loam and a silty clay. Hydraulic properties of the two soil types were derived from Rijtema (1969) using semi-empirical relations between soil suction and hydraulic conductivity. The resulting functions are given in tabulated form in the listing of the model (Appendices 6.1 and 6.2). For both soil types runs were made with evaporative demands of 4, 6 and 9 mm.d⁻¹, introduced as forcing functions.

In all cases the profile started at an equilibrium situation, assuming an initial groundwater table at 0.3 m below soil surface. The moisture contents at saturation for clay loam and silty clay are 0.445 and 0.504 cm³.cm⁻³, respectively.

The distribution of soil moisture in the profile after 5, 10 and 30 days of evaporation at the three evaporativities is shown in Fig. 6.5. As can be expected, the soil moisture content of the surface layers decreases with the increasing evaporative demand.

After 30 days of evaporation, when the soil has started to dry up at the surface, the difference in soil moisture in the top layers for three evaporation rates becomes small (Fig. 6.6). The cumulative water losses are 80, 90 and 92 mm for evaporative demands of 4, 6 and 9 mm.d⁻¹ respectively (Fig. 6.7). Hence, despite more than a factor 2 difference in evaporative demand, there is only 15 percent difference in cumulative evaporation, because of the difference in drying out of the top layers and its depressing effect on soil surface evaporation. As the topsoil dries out, transport of water from the profile to the atmosphere is increasingly hampered and the evaporation rate declines. The dry surface acts as a barrier to further evaporation (mulch effect).

The simulated distribution of soil moisture in the profile for the two soils is given in Fig. 6.8. Higher moisture contents are found in silty clay.

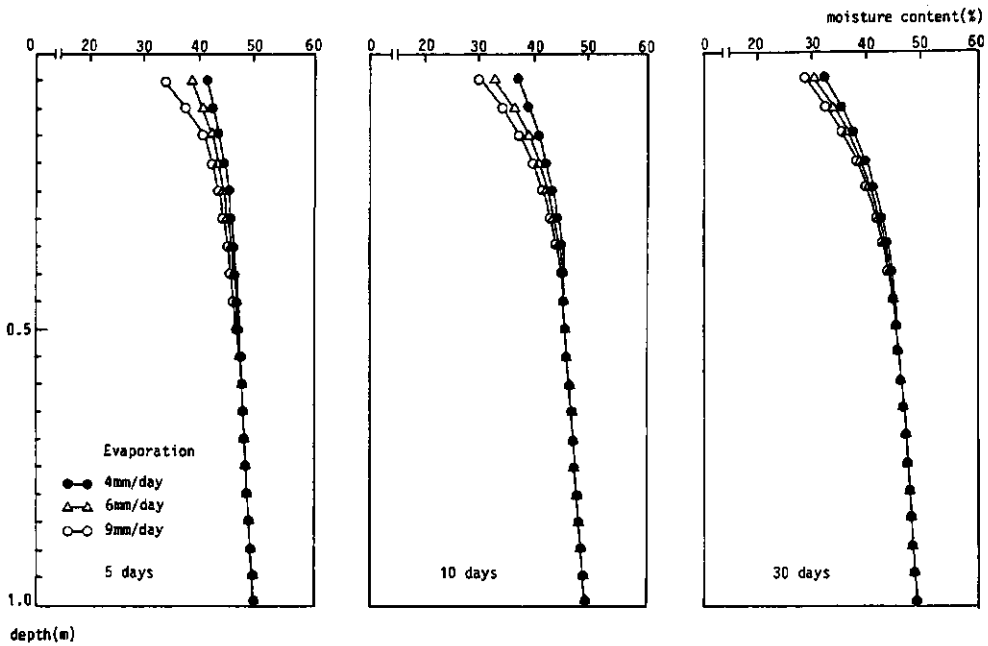


Fig. 6.5 The distribution of soil moisture at different depths along the profile of a clay loam soil under three evaporation rates.

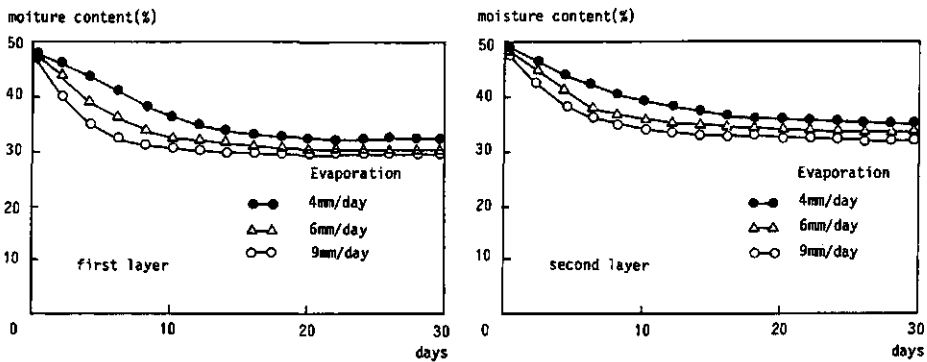


Fig. 6.6 The changes of soil moisture of the first and second layers with time under different evaporative demands for clay loam soil.

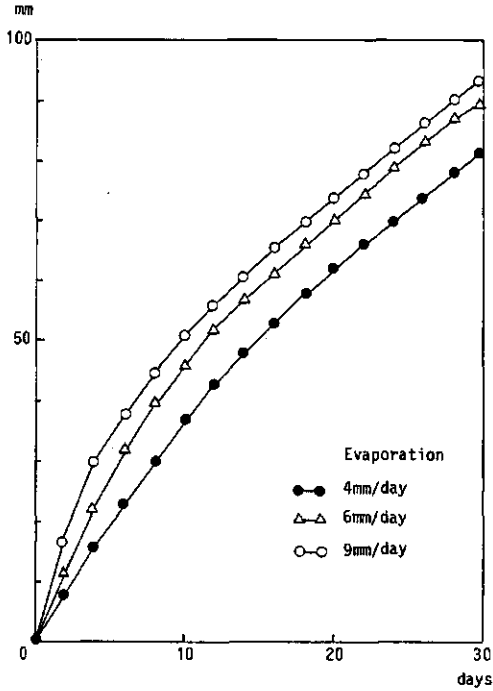


Fig. 6.7 The cumulative evaporation under three evaporation rates for clay loam soil.

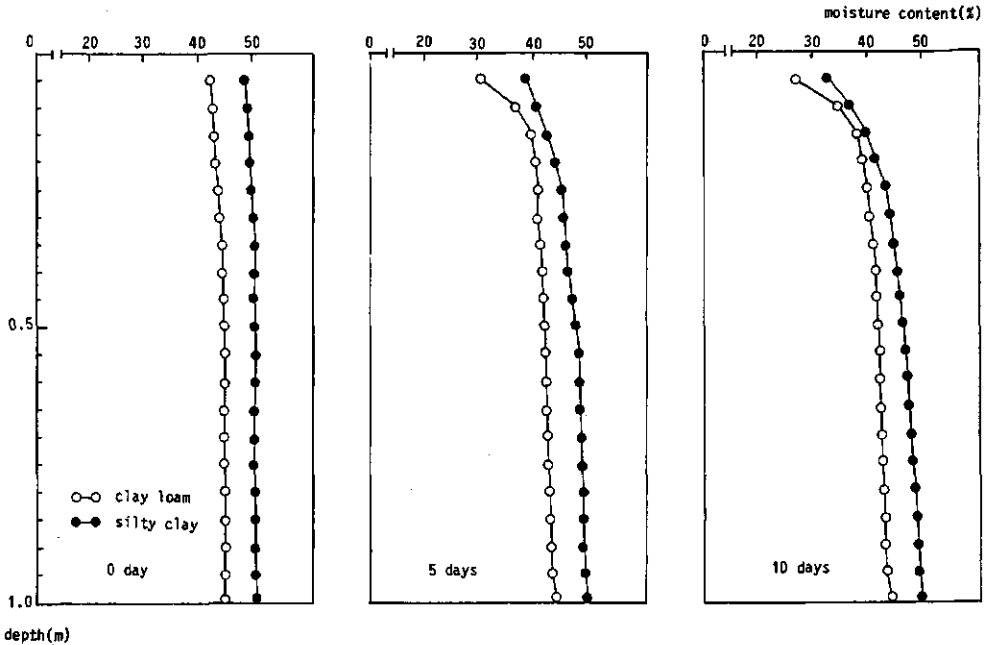


Fig. 6.8 The moisture content of different depths for two soil types after 0, 5 and 10 days of evaporation (6 mm/day).

Table 6.1 The concentration of O_2 in clay loam over time at an evaporative demand of 4 mm/d.

days	0	5	10	20	30
depth (cm)					
0- 5	2.0 E-4	2.0 E-4	2.0 E-4	2.1 E-4	2.1 E-4
5- 10	2.0 E-4	2.0 E-4	2.0 E-4	2.0 E-4	2.0 E-4
10- 15	2.0 E-4	1.8 E-4	1.8 E-4	1.8 E-4	1.8 E-4
15- 20	2.0 E-4	1.5 E-4	1.5 E-4	1.5 E-4	1.5 E-4
20- 25	2.0 E-4	1.1 E-4	1.1 E-4	1.1 E-4	1.1 E-4
25- 30	<u>2.0 E-4</u>	5.7 E-5	5.7 E-5	5.7 E-5	5.7 E-5
30- 35		2.8 E-8	6.3 E-8	1.3 E-7	1.5 E-7
35- 40		6.6 E-12	3.2 E-11	1.4 E-10	3.2 E-10
40- 45		1.0 E-15	1.0 E-14	9.6 E-14	3.4 E-13
45- 50		1.1 E-19	2.4 E-18	4.8 E-17	2.6 E-16
50- 55		8.6 E-24	7.3 E-22	1.9 E-20	1.6 E-19
55- 60		5.6 E-28	1.2 E-25	5.8 E-24	7.5 E-23
60- 65		<u>2.6 E-32</u>	<u>1.6 E-29</u>	1.5 E-27	3.0 E-26
65- 70				<u>3.2 E-31</u>	1.0 E-29
70- 75					
75- 80					
80- 85					
85- 90					
90- 95					
95-100					

The simulated time course of concentration of O_2 at different depths in the profile is given in Table 6.1 for the clay loam. As evaporation proceeds, the depth of the groundwater increases, the moisture content in the profile decreases and oxygen has the opportunity to enter the unsaturated layers of the soil profile. The increase in overall oxygen concentration is the result of a higher proportion of air filled pores in the soil. There is hardly any difference in oxygen concentration

Table 6.3 The production of sulphate (kg/m^3) in clay loam soil (SUCT_1 , COND_2) at different evaporation rates.

days EV(mm/day)	5 days			10 days		
	4	6	9	4	6	9
depth (cm)						
0- 5						
5- 10						
10- 15						
15- 20						
25- 30						
30- 35	8.1 E-12	8.3 E-12	1.0 E-11	1.2 E-11	1.7 E-11	1.6 E-11
35- 40	4.3 E-15	6.9 E-15	7.0 E-15	1.6 E-14	1.9 E-14	1.9 E-14
40- 45	9.8 E-19	1.3 E-18	1.5 E-18	6.9 E-18	9.5 E-18	8.7 E-18
45- 50	1.4 E-22	1.7 E-22	2.1 E-22	2.1 E-21	2.6 E-21	2.5 E-21
50- 55	1.4 E-26	1.6 E-26	2.1 E-26	4.4 E-25	5.5 E-25	5.7 E-25
55- 60	9.9 E-31	1.1 E-30	1.6 E-30	7.2 E-29	8.7 E-29	9.4 E-29
60- 65	<u>5.6 E-35</u>	<u>6.6 E-35</u>	<u>9.8 E-35</u>	9.3 E-33	1.1 E-32	1.1 E-32
65- 70				<u>9.9 E-37</u>	<u>1.1 E-36</u>	<u>1.3 E-36</u>
70- 75						
75- 80						
80- 85						
85- 90						
90- 95						
95-100						

only marginally affected by different evaporative demands.

The model presented in this chapter is only a first step towards the development of a truly comprehensive model for the oxidation and acidification processes in acid sulphate soils, that could eventually be used to formulate recommendations for management and reclamation of these soils.

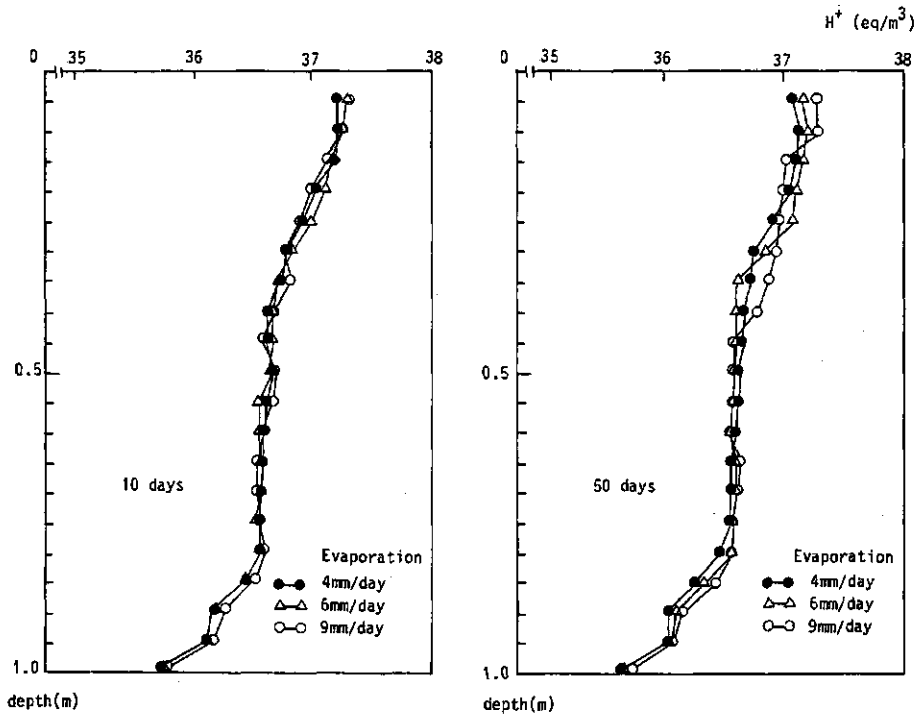


Fig. 6.10 The concentration of hydrogen at different depths under three evaporation regimes after 10 and 50 days of evaporation for clay loam soil.

6.10 References

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Appendix 6.1 Listing of program on simulation of oxidation and acidification processes in acid sulphate soils

```

DIMENSION ACOND(21), DFLCA(21), APDIFC(21)
DIMENSION MFLCA(21), DFLH(21), APDIFH(21), MFLH(21)
DIMENSION APDIF(21), DFLSO(21), CAL(21)
DIMENSION MFLSO(21), ADEF(21)
DIMENSION DFLMG(21), APDIFM(21), MFLMG(21), MFLK(21)
DIMENSION MFLAL(21), APDIFA(21), DFLAL(21)
DIMENSION MFLNA(21), APDIFN(21), DFLNA(21)
STORAGE DEF(21), PSO4(21), DEFAC(21), RCOX(21), CHYD(21),...
      CCA(21), RPHYD(21), RFLOX(21), WC(21)
STORAGE RFLOW(21), PSI(21), SUCT(21), IPSI(21), COND(21),...
      COX(21), CSO4(21), DEPTH(21), DIFD(21),...
      ITCOM(21), WCI(21), AMGI(21), AALI(21), AKI(21)
STORAGE APDIFK(21), DFLK(21), CMG(21),...
      CK(21), KI(21), CAI(21), MGI(21), HI(21),...
      ALI(21), MFLOX(21), DFLOX(21),...
      NAI(21) CNA(21), ANAI(21),...
      CEC(21), ACAI(21), AHYDI(21), TCOM(21), NFW(21)

*TITLE ACID SULPHATE SOILS
*UNIT M-KG-DAY
INITIAL
NOSORT
* DEFINE INVARIABLE GEOMETRY
TABLE ITCOM(1-20)=20x.05
*TABLE FOR EXCHANGED CATIONS EQUIVALENT/M3
TABLE HI(1-20)=20x20.
TABLE MGI(1-20)=20x30.
TABLE KI(1-20)=20x50.
TABLE ALI(1-20)=20x50.
TABLE NAI(1-20)=20x60.
TABLE CAI(1-20)=20x200.
PARAM NC=20
PARAM CHYDI=0.001, CCAI=0.025, CSO4I=.1411, COXI=2.E-4
PARAM CNAI=0.04, CALI=0.0001

```

```

PARAM CKI=0.050, CMGI=.025
FIXED N5,I,IM,N,N1,N2,N3,N4,NC,II,J,JJ,K,KM,KJ,MM,KK,NP,NS,M
FIXED N6,N7
    DO 201 I=1,20
201  TCOM(I)=ITCOM(I)
    DIFD(1)=.5*TCOM(1)
    DEPTH(1)=.5*TCOM(1)
    DO 11 I=2,20
    DIFD(I) = (TCOM(I-1)+TCOM(I))*0.5
    DEPTH(I) = DEPTH(I-1)+DIFD(I)
11  CONTINUE
    DO 999 I=1,NC
    IPSI(I)=DPGWT-DEPTH(I)
999  CONTINUE
    DO 998 I=1,NC
    WCI(I)=AFGEN(PSIT1,IPSI(I)
    IF(WCI(I).GE.PVOL)WCI(I)=PVOL
998  CONTINUE
    DO 22 I = 1,NC
    AMWI(I)=WCI(I)*TCOM(I)
    ACAI(I)=AMWI(I)*CCAI
    ASO4I(I)=AMWI(I)*CSO4I
    AMOXI(I)=COXI*(TCOM(I)*(PVOL-WCI(I)))
    AHYDI(I)=AMWI(I)*CHYDI
    AMGI(I)=AMWI(I)*CMGI
    AKI(I)=AMWI(I)*CKI
    ANAI(I)=AMWI(I)*CNAI
    AALI(I)=AMWI(I)*CALI
    CEC(I)=(HI(I)+MGI(I)+KI(I)+NAI(I)+ALI(I)+CAI(I))*TCOM(I)
    THYDI(I)=HI(I)*TCOM(I)+AHYDI(I)
    TCAI(I)=ACAI(I)+TCOM(I)*CAI(I)
    TMGI(I)=AMGI(I)+TCOM(I)*MGI(I)
    TKI(I)=AKI(I)+TCOM(I)*KI(I)
    TNAI(I)=ANAI(I)+TCOM(I)*NAI(I)
    TALI(I)=AAL.I(I)+TCOM(I)*ALI(I)
22  CONTINUE

```

PARAM DEVEAP = 0.004, PI = 3.1416

*DAILY EVAPORATION

PARAM WCLIM = 0.25, WCFC = 0.39

FUNCTION CONDT1 = (0.059, 6.7E-11), (0.177, 6.4E-10), ...
 (0.2, 1.7E-9), (0.22, 4.5E-9), (0.247, 9.5E-9), ...
 (.255, 2.2E-8), (0.277, 4.2E-8), (0.308, 1.1E-7), ...
 (0.342, 1.75E-7), (0.345, 4.04E-7), (0.349, 6.04E-7), ...
 (0.35, 1.06E-6), ...
 (0.36, 1.59E-6), (0.366, 2.81E-6), (0.37, 3.36E-6), ...
 (0.372, 3.84E-6), (0.374, 4.13E-6), (0.377, 4.82E-6), ...
 (0.38, 0.58E-5), (0.383, 0.96E-5), (0.385, 1.99E-5), ...
 (0.387, 2.55E-5), (0.389, 4.18E-5), (0.393, 6.87E-5), ...
 (0.395, 1.12E-4), (0.398, 1.85E-4), (0.4, 2.37E-4), ...
 (0.402, 3.04E-4), (0.404, 3.89E-4), (0.406, 6.53E-4), (0.411, ...
 8.2E-4), (0.412, 1.3E-3), (0.414, 1.7E-3), (0.415, 2.2E-3), ...
 (0.416, 2.8E-3), (0.421, 4.5E-3), (0.429, 7.6E-3), ...
 (0.437, 9.2E-3), (0.445, 9.8E-3)

FUNCTION SUCT1 = (0.059, 10000), (0.177, 2000), (0.2, 1000), ...
 (0.22, 500), (0.247, 200), (0.255, 160), (0.277, 100), ...
 (0.308, 50), (0.342, 25), (0.345, 20), (0.349, 15), ...
 (0.355, 10), (0.36, 7.5), (0.366, 5.0), (0.368, 4.8), ...
 (0.37, 4.4), (0.372, 4.), (0.374, 3.8), (0.377, 3.4), ...
 (0.38, 3.0), (0.383, 2.8), (0.385, 2.5), (0.387, 2.4), ...
 (0.389, 2.2), (0.393, 2.), (0.395, 1.8), (0.398, 1.6), ...
 (0.40, 1.5), (0.402, 1.4), (0.404, 1.3), (0.406, 1.2), ...
 (0.411, 1.), (0.412, 0.8), (0.414, 0.7), ...
 (0.415, 0.6), (0.416, 0.5), (0.417, 0.4), (0.421, 0.311), ...
 (0.429, 0.1), (0.437, 0.025), (0.445, 0.0)

FUNCTION CONDT2 = (0.065, 1.1E-9), (0.182, 1.06E-8), ...
 (0.203, 2.82E-8), (.225, 7.44E-8), (0.252, 2.7E-7), ...
 (0.257, 3.7E-7), (0.283, 7.1E-7), (0.318, 1.9E-6), ...
 (0.352, 4.9E-6), (0.363, 6.7E-6), (0.375, 1.E-5), ...
 (0.392, 1.8E-5), (0.405, 2.7E-5), (0.42, 4.7E-5), ...
 (0.43, 6.9E-5), (0.435, 8.1E-5), (0.436, 9.6E-5), ...
 (0.438, 1.E-4), (0.44, 1.1E-4), (0.443, 1.3E-4), ...
 (0.445, 1.5E-4), (0.447, 1.7E-4), (0.449, 1.9E-4), ...

```
(0.452,2.3E-4),(0.457,3.5E-4),(0.46,3.9E-4),...
(0.463,4.4E-4),(0.466,6.1E-4),(0.468,7.3E-4),...
(0.471,9.E-4),(0.474,1.2E-3),(0.477,1.9E-3),...
(0.482,2.9E-3),(0.492,8.E-3),(0.5,1.15E-2),...
(0.507,1.3E-2)
```

```
FUNCTION SUCT2 = (0.065,10000),(0.182,2000),...
(0.203,1000),(0.225,500),(0.252,200),(0.257,160),...
(0.283,100),(0.318,50),(0.352,25),(0.363,20),...
(0.375,15),(0.392,10),(0.405,7.5),(0.42,5.),...
(0.43,3.8),(0.435,3.4),(0.436,3.), (0.438,2.8),...
(0.44,2.6),(0.443,2.4),(0.445,2.2),(0.447,2.),...
(0.449,1.8),(0.452,1.6),(0.455,1.4),(0.457,1.2),...
(0.46,1.1),(0.463,1.), (0.464,0.9), (.466,0.8),...
(0.471,0.6),(0.474,0.5),(0.477,0.4),(0.482,0.31),...
(0.492,0.1),(0.5,0.025),(0.504,0.0)
```

```
FUNCTION PSIT1 = -30.,1.5,0.,0.445,0.025,0.437,0.1,0.429,...
0.31,0.421,0.4,0.417,0.5,0.416,0.6,0.415,0.7,0.414,...
0.8,0.412,1.,0.411,1.2,0.406,1.3,0.404,1.4,0.402,...
1.5,0.4,1.6,.398,1.8,.395,2.,.393,2.2,.389,...
2.4,.387,2.8,.383,3.,.38
```

```
FUNCTION PSIT2 = -30.,1.5,0.,.504,.025,0.5,0.1,.492,0.31,.482,.4,...
.477,.5,.474,.6,.471,.8,.466,.9,.464,1.,.463,1.1,.46,...
1.2,.457,1.4,.455,1.6,.452,1.8,.449,2.,.447,...
2.2,.445,2.4,.443,2.6,.44,3.8,.43
```

```
PARAM DWC=1.
```

```
*MOISTURE CONTENT TO BE REMOVED BEFORE GW SHIFTS
```

```
PARAM PVOL = 0.445
```

```
*TOTAL PORE VOLUME IN M3/M3
```

```
DYNAMIC
```

```
NOSORT
```

```
CONSAT = AFGEN(CONDT1,PVOL)
```

```
DO 59 I = 1,NC
```

```
WC(I) = AMW(I)/TCOM(I)
```

```
IF(WC(I).GE.PVOL)WC(I)=PVOL
```

```
CSO4(I) = ASO4(I)/AMW(I)
```

```
DO 55 J = 1,NC
```

```

IM = J
IF(WC(J).GE.PVOL) GO TO 54
COX(J) = AMOX(J)/(ITCOM(J)* (PVOL-WC(J)))
55 CONTINUE
GO TO 53
54 CONTINUE
DO 52 K = IM,NC
COX(K) = 0
52 CONTINUE
53 CONTINUE
59 CONTINUE
N=(DPGWT/0.04999)+1.
IF(N.LT.5)STOP
IPSI(N-1)=DPGWT-DEPTH(N-1)
IF(N.GT.21)STOP
WC(N-1)=AFGEN(PSIT1,IPSI(N-1))
WC(N)=PVOL
*DEFINITION OF MOISTURE FLOW, UNSATURATED
*DOWNWARD FLOW IS POSITIVE
DO 58 I = 1,NC
COND(I) = AFGEN(CONDT1,WC(I))
SUCTION(I) = AFGEN(SUCT1,WC(I))
58 CONTINUE
ACOND(1) = COND(1)
PSI(1) = -SUCTION(1)+DPGWT-DEPTH(1)
DO 57 I = 2,NC
ACOND(I) = (COND(I-1)+COND(I))*0.5
PSI(I) = -SUCTION(I)+DPGWT-DEPTH(I)
57 CONTINUE
FUNCTION REDFDT = -1.5,0.0,.075,.05,.1,.1,.2,.2,.375,.3,...
.5,.4,.725,.5,.775,.75,.9,1.,1.,1.1,1.,2.,1.
WCPR = (WC(1)-WCLIM)/(WCFC-WCLIM)
IF(WCPR.LT.0.)WCPR=0
REDFD = AFGEN(REDFDT,WCPR)
AMP=DEVAP*PI
EVAPO = AMX1(0.0001,AMP*(SIN(2.*PI*TIME)))*REDFD

```



```

      RFLOW(1) = -EVAPO
*GROUNDWATER TABLE
INCON DPGWT = .30
      N = (DPGWT/0.04999)+1.
      J=N
      JJ=NC+1
      DO 97 I = J,JJ
        RFLOW(I) = RFLOW(I-1)
97 CONTINUE
      KM = N-1
      DO 95 I = 2,KM
        RFLOW(I) = ACOND(I)*(PSI(I-1)-PSI(I))/DIFD(I)
        IF(ABS(RFLOW(I)).LT.0.01*DELT)RFLOW(I)=0.0
95 CONTINUE
      AMW = INTGRL(AMWI,RNFLW,20)
      DO 96 I = 1,NC
        NFLW(I) = RFLOW(I)-RFLOW(I+1)
96 CONTINUE
SORT
PROCEDURE RNFLW,DELW1,DELW,RFLOW,TCOM,DELXX,PSI = ALGBR(DPGWT,...
      SUCT,NFLW,DELX)
      IF(DPGWT.LT.1.)DELW=0.0
      IF(DPGWT.GE.1.)GO TO 121
      DO 101 I=1,NC
        DELW=DELW+NFLW(I)*DELT
101 CONTINUE
      IF(ABS(DELW).GT.0.004*DELT) GO TO 102
      GO TO 109
102 DPGWT = DPGWT-DELW*0.2
      IF(DPGWT.GE.1.)DPGWT=1.
121 N=(DPGWT/0.04999)+1.
      IF(N.LT.5)STOP
      ETCOM=TCOM(N-1)
      EWC=WC(N-1)
      TCOM(N-2)=ITCOM(N-2)
      DEPTH(N-2)=DEPTH(N-3)+0.5*(TCOM(N-2)+TCOM(N-3))

```

```

104 TCOM(N-1)=DPGWT-DEPTH(N-2)-0.5*TCOM(N-2)
   DEPTH(N-1)=DEPTH(N-2)+0.5*(TCOM(N-2)+TCOM(N-1))
   N1=N-4
   N5=N-3
   N6=N-5
   N2=N-1
   N7=N2-1
   DO 133 I=N1,N7
   AMW(I)=AMW(I)
   WC(I)=WC(I)
133 CONTINUE
   PSI(N1-1)=-SUCT(N1-1)+DPGWT-DEPTH(N1-1)
   IPSI(N-1)=DPGWT-DEPTH(N-1)
   WC(N-1)=AFGEN(PSIT1,IPSI(N-1))
   DO 132 I=N1,N2
   SUCT(I)=AFGEN(SUCT1,WC(I))
   COND(I)=AFGEN(CONDT1,WC(I))
   ACOND(I)=(COND(I)+COND(I-1))*0.5
132 CONTINUE
   DO 106 I=N1,N2
   DIFD(I)=(TCOM(I)+TCOM(I-1))*0.5
   PSI(I)=-SUCT(I)+DPGWT-DEPTH(I)
106 CONTINUE
   DO 114 I=N1,N2
   RFLOW(I)=ACOND(I)*(PSI(I-1)-PSI(I))/DIFD(I)
   IF(ABS(RFLOW(I)).LT.0.01*DELT)RFLOW(I)=0.0
114 CONTINUE
   IF(N.EQ.21) GO TO 111
111 N3=NC+1
   DO 115 I=N,N3
   RFLOW(I)=RFLOW(I-1)
115 CONTINUE
   DO 107 I=N1,N
   NFLW(I)=RFLOW(I)-RFLOW(I+1)
107 CONTINUE
   IF(N.FQ.21) GO TO 109

```

```

DELX=0.0
DO 108 I=N1,N
DELX=DELX+NFLW(I)*DELT
108 CONTINUE
DELXX=DELX+(WC(N-1)-EWC)*ETCOM+(WC(N-1)-...
PVOL)*(TCOM(N-1)-ETCOM)
DELW1=DELW
DELW=DELW-DELXX
IF (ABS(DELXX).GT.ABS(DELW1)) GO TO 109
IF (ABS(DELW).LT.0.002*DELT) GO TO 109
DO 131 I=N1,N7
AMW(I)=AMW(I)+NFLW(I)*DELT
WC(I)=AMW(I)/TCOM(I)
131 CONTINUE
GO TO 102
109 CONTINUE
DO 110 I=1,NC
RNFLW(I)=NFLW(I)
110 CONTINUE
ENDPRO
*MOVEMENT OF SULPHATE
NOSORT
DO 89 I=2,NC
MFLSO(I) = RFLOW(I)*.5*(CSO4(I)+CSO4(I-1))
APDIF(I) = DNOT*WC(I)*TORT/DIFD(I)+ABS(RFLOW(I))*DISP
DFLSO(I) = APDIF(I)*(CSO4(I-1)-CSO4(I))
89 CONTINUE
PARAM DNOT = 6.5E-5,TORT = .7,DISP = .03
MFLSO(1) = RFLOW(1)*CSO4(1)
APDIF(1) = DNOT*WC(1)*TORT/DIFD(1)+ABS(RFLOW(1))*DISP
DFLSO(1) = 0.0
DO 86 I=N,N3
MFLSO(I) = MFLSO(I-1)
DFLSO(I) = DFLSO(I-1)
86 CONTINUE
ASO4=INTGRL(ASO4I,NFSO4,20)

```

```

DO 79 I=1,NC
DEFAC(I) = AFGEN(DEFACT,(PVOL-WC(I)))
DEF(I) = DEFAC(I)*DZERO
79 CONTINUE
IF(N.LE.NC) GO TO 71
IF(N.GT.NC)N=NC
GO TO 71
71 DO 78 I=2,KM
ADEF(I) = (DEF(I)+DEF(I-1))*0.5
DFLOX(I)=ADEF(I)*(COX(I-1)-COX(I))/DIFD(I)
78 CONTINUE
DFLOX(1) = DEF(1)*(COUT-COX(1))/DIFD(1)
KK = N-1
KJ=N-2
DO 77 I=N,JJ
DFLOX(I) = 0.0
MFLOX(I) = 0.0
77 CONTINUE
DO 72 I=1,KK
RFLOX(I) = DFLOX(I)+MFLOX(I)
72 CONTINUE
DO 76 I=1,KJ
MFLOX(I)=RNFLW(I)*COX(I)
78 CONTINUE
MFLOX(N-1)=RFLW(N-1)*COX(N-1)
DO 74 I=N,JJ
MFLOX(I)=RNFLW(I)*COX(I)
74 CONTINUE
*PRODUCTION OF SULPHATE
FUNCTION DEFACT = 0.00,0.00001,.01,.00005,.10,.002,.13,.0343,...
.139,.0441,...
.16,.0669,.168,.0781,.176,.089,.184,.0975,.20,.1165,...
.211,.1206,.216,.122,.227,.1234,.245,.1242,...
.329,.1316,.395,.144,.460,.1579,.531,.167
PARAM PYRL = 0.3
NP=(PYRL/0.04999)+1.

```

```

      N4=NP-1
      IF(N.GT.NP) GO TO 84
      PSO4(N)=0.0
      RCOX(N)=0.0
      GO TO 87
84  NS=N-1
      DO 83 I=NP,NS
      IF(RFLOX(I).LE.0.0)FX=0.0
      IF(RFLOX(I).GT.0.0)FX=1.0
      PSO4(I)=FXx0.4xRFLOX(I)x1.6
      RCOX(I)=FXx0.4.RFLOX(I)
83  CONTINUE
87  DO 81 I=1,N4
      PSO4(I)=0.0
      RCOX(I)=0.0
81  CONTINUE
      DO 85 I=N,JJ
      PSO4(I)=0.0
      RCOX(I)=0.0
85  CONTINUE
      DO 70 I=1,NC
      NFLOX(I)=DFLOX(I)-DFLOX(I+1)-MFLOX(I)-RCOX(I)
70  CONTINUE
      DO 88 I=1,N7
      NFSO4(I)=MFLSO(I)-MFLSO(I+1)+DFLSO(I)-DFLSO(I+1)+PSO(I)
88  CONTINUE
      NFSO4(N6)=-RFLOW(N6)x(CSO4(N6)-CSO4(N6+1))+...
      DFLSO(N6)-DFLSO(N6+1)+PSO4(N6)
      NFSO4(N1)=-RFLOW(N1+1)x(CSO4(N1)-CSO4(N1+1))+...
      DFLSO(N1)-DFLSO(N1+1)+PSO4(N1)
      DO 880 I=N5,NC
      NFSO4(I)=MFLSO(I)-MFLSO(I+1)+DEFLSO(I)-DFLSO(I+1)+PSO4(I)
880  CONTINUE
      AMOX = INTGRI (AMOXI,NFLOX,20)
PARAM DZERO = 2.26E-5,COUT = 2.75E-4
PARAM TAK=+1.0

```

```

PARAM EPS=0.000001
PARAM ALPH2=0.2,BETA2=0.4,CD=0.25
*      H/K      CA/MG      KD1/KM1
PARAM ALPH3=0.5,SIGMA=0.37
*      H/NA      NA/AL
FIXED IER,IK,IEPS
*      ACIDITY OF SOIL COMPARTMENTS
PARAM DNOTH = 3.0E-4,DNOTCA = 1.03E-4
PARAM DNOTAL=1.5E-4,DNOTNA=1.3E-4
PARAM DNOTMG=0.61E-4,DNOTK=1.64E-4
      DO 69 I=1,NC
      RPHYD(I) = PS04(I)*0.0208
69 CONTINUE
      DO 68 I=1,NC
      TM3 = AHYD(I)/ITCOM(I)
      TM1=ANA(I)/ITCOM(I)
      TD1 = ACA(I)/ITCOM(I)
      TM2=AK(I)/ITCOM(I)
      TD2=AMG(I)/ITCOM(I)
      TT1=AAL(I)/ITCOM(I)
      CECE=CEC(I)
      XST=TM1/10
      IF(TAK.LT.0.)XST=CNA(I)
      IF(XST.LT.1.F-20)XST=TD1/10
Z,IER,IK,IEPS=RINI(FF,DERF,XST,EPS,20,IM1,IM2,IDO,CD,TD2,...
                  CECE,ALPH2,BETA2,IM3,TT1,SIGMA,ALPH3)
*CALCULATION OF RESULTING CONCENTRATIONS
      X1=Z
      Y1=CD*XZ*Z
      X2=ALPH2*XZ
      X3=ALPH3*XZ
      Y2=BETA2*Y1
      Y3=SIGMA*XZ*XZ*Z
      CHYSOL=X3*TM3/(1.+X3)
      CHYD(I)=CHYSOL
      CALSOL=Y3*TT1/C1.+Y3)

```

```

CAL(I)=CALSOL/WC(I)
ALI(I)=TT1-CALSOL
CNASOL=X1*TM1/(1.+X1)
CNA(I)=CNASOL/WC(I)
NAI(I)=TM1-CNASOL
CKSOL=X2*TM2/(1.+X2)
CK(I)=CKSOL/WC(I)
KI(I)=TM2-CKSOL
CCASOL=Y1*TD1/(1.+Y1)
CCA(I)=CCASOL/WC(I)
CAI(I)=TD1-CCASOL
CMGSOL=Y2*TD2/(1.+Y2)
CMG(I)=CMGSOL/WC(I)
MGI(I)=TD2-CMGSOL

```

68 CONTINUE

*BOUNDARY CONDITION

```

DFLAL(1)=0.0
DFLNA(1)=0.0
DFLH(1)=0.0
DFLCA(1)=0.0
DFLMG(1)=0.0
DFLK(1)=0.0
CAL(21)=CAL(20)
CNA(21)=CNA(20)
CHYD(21)=CHYD(20)
CCA(21)=CCA(20)
CMG(21)=CMG(20)
CK(21)=CK(20)
MFLH(1)=RFLOW(1)*CHYD(1)
MFLCA(1)=RFLOW(1)*CCA(1)
MFLNA(1)=RFLOW(1)*CNA(1)
MFLAL(1)=RFLOW(1)*CAL(1)
MFLMG(1)=RFLOW(1)*CMG(1)
MFLK(1)=RFLOW(1)*CK(1)
DO 67 I=2,NC
MFLH(I) = RFLOW(I)*.5*(CHYD(I)+CHYD(I-1))

```

```

APDIFH(I) = DNOTHxWC(I)xTORT/DIFD(I)+ABS(RFLOW(I))xDISP
DFLH(I) = APDIFH(I)x(CHYD(I-1)-CHYD(I))
MFLCA(I) = RFLOW(I)x0.5x(CCA(I)+CCA(I-1))
APDIFC(I) = DNOTCAxWC(I)xTORT/DIFD(I)+ABS(RFLOW(I))xDISP
DFLCA(I) = APDIFC(I)x(CCA(I-1)-CCA(I))
MFLMG(I)=RFLOW(I)x0.5x(CMG(I)+CMG(I-1))
APDIFM(I)=DNOTMGxWC(I)xTORT/DIFD(I)+ABS(RFLOW(I))xDISP
DFLMG(I)=APDIFM(I)x(CMG(I-1)-CMG(I))
MFLK(I)=RFLOW(I)x0.5x(CK(I)+CK(I-1))
APDIFK(I)=DNOTKxWC(I)xTORT/DIFD(I)+ABS(RFLOW(I))xDISP
DFLK(I)=APDIFK(I)x(CK(I-1)-CK(I))
MFLAL(I)=RFLOW(I)x0.5x(CAL(I)+CAL(I-1))
APDIFA(I)=DNOTALxWC(I)xTORT/DIFD(I)+ABS(RFLOW(I))xDISP
DFLAL(I)=APDIFA(I)x(CAL(I-1)-CAL(I))
MFLNA(I)=RFLOW(I)x0.5x(CNA(I)+CNA(I-1))
APDIFN(I)=DNOTNAxWC(I)xTORT/DIFD(I)+ABS(RFLOW(I))xDISP
DFLNA(I)=APDIFN(I)x(CNA(I-1)-CNA(I))

```

67 CONTINUE

```

DO 61 I=N,N3
MFLAL(I)=MFLAL(I-1)
DFLAL(I)=DFLAL(I-1)
MFLNA(I)=MFLNA(I-1)
DFLNA(I)=DFLNA(I-1)
MFLH(I) =MFLH(I-1)
DFLH(I) =DFLH(I-1)
MFLCA(I)=MFLCA(I-1)
DFLCA(I)=DFLCA(I-1)
MFLK(I)=DFLK(I-1)
MFLMG(I)=MFLMG(I-1)
DFLMG(I)=DFLMG(I-1)

```

61 CONTINUE

```

DO 66 I=1,N7
NFLHYD(I)=MFLH(I)-MFLH(I+1)+DFLH(I)-DFLH(I+1)+RPHYD(I)
NFLCA(I)=MFLCA(I)-MFLCA(I+1)+DFLCA(I)-DFLCA(I+1)
NFLMG(I)=MFLMG(I)-MFLMG(I+1)+DFLMG(I)-DFLMG(I+1)
NFLK(I)=MFLK(I)-MFLK(I+1)+DFLK(I)-DFLK(I+1)

```


NFLAL(I)=MFLAL(I)-MFLAL(I+1)+DFLAL(I)-DFLAL(I+1)

NFLNA(I)=MFLNA(I)-MFLNA(I+1)+DFLNA(I)-DFLNA(I+1)

66 CONTINUE

NFLHYD(N6)=-RFLOW(N6)x(CHYD(N6)-CHYD(N6+1))+...

DFLH(N6)-DFLH(N6+1)+RPHYD(N6)

NFLHYD(N1)=-RFLOW(N1+1)x(CHYD(N1)-CHYD(N1+1))+...

DFLH(N1)-DFLH(N1+1)+RPHYD(N1)

NFLCA(N6)=-RFLOW(N6)x(CCA(N6)-CCA(N6+1))+...

DFLCA(N6)-DFLCA(N6+1)

NFLCA(N1)=-RFLOW(N1+1)x(CCA(N1)-CCA(N1+1))+...

DFLCA(N1)-DFLCA(N1+1)

NFLMG(N1)=-RFLOW(N1+1)x(CMG(N1)-CMG(N1+1))+...

DFLMG(N1)-DFLMG(N1+1)

NFLMG(N6)=-RFLOW(N6)x(CMG(N6)-CMG(N6+1))+...

DFLMG(N6)-DFLMG(N6+1)

NFLK(N6)=-RFLOW(N6)x(CK(N6)-CK(N6+1))+DFLK(N6)-DFLK(N6+1)

NFLK(N1)=-RFLOW(N1+1)x(CK(N1)-CK(N1+1))+...

DFLK(N1)-DFLK(N1+1)

NFLAL(N6)=-RFLOW(6)x(CAL(N6)-CAL(N6+1))+...

DFLAL(N6)-DFLAL(N6+1)

NFLAL(N1)=-RFLOW(N1+1)x(CAL(N1)-CAL(N1+1))+...

DFLAL(N1)-DFLAL(N1+1)

NFLNA(N6)=-RFLOW(N6)x(CNA(N6)-CNA(N6+1))+...

DFLNA(N6)-DFLNA(N6+1)

NFLNA(N1)=-RFLOW(N1+1)x(CNA(N1)-CNA(N1+1))+...

DFLNA(N1)-DFLNA(N1+1)

DO 669 I=N5,NC

NFLHYD(I)=MFLH(I)-MFLH(I+1)+DFLH(I)-DFLH(I+1)+RPHYD(I)

NFLCA(I)=MFLCA(I)-MFLCA(I+1)+DFLCA(I)-DFLCA(I+1)

NFLMG(I)=MFLMG(I)-MFLMG(I+1)+DFLMG(I)-DFLMG(I+1)

NFLK(I)=MFLK(I)-MFLK(I+1)+DFLK(I)-DFLK(I+1)

NFLAL(I)=MFLAL(I)-MFLAL(I+1)+DFLAL(I)-DFLAL(I+1)

NFLNA(I)=MFLNA(I)-MFLNA(I+1)+DFLNA(I)-DFLNA(I+1)

669 CONTINUE

AHYD = INTGR(THYDI,NFLHYD,20)

AAI=INTGRI(TALI,NFLAL,20)

```

ANA=INTGRL(TNAI,NFLNA,20)
ACA=INTGRL(TCAI,NFLCA,20)
AMG=INTGRL(IMGI,NFLMG,20)
AK=INTGRL(TKI,NFLK,20)
TEVAPO=INTGRL(0.,EVAPO)
TIMER FINTIM = 30.,OUTDEL=1.,PRDEL=1.,DELT=0.001
METHOD RECT

PRINT CHYD(1-20),COX(1-20),...
      DPGWT,TEVAPO,DELW,DELXX
OUTPUT WC(1-20), NFLOX(1-20)
OUTPUT RFLOW(1-20),PSO4(1-20)
NOSORT
      IF(KEEP.EQ.0) GO TO 700
      IF(IMPULS(0.,PRDEL).LT.0.5) GO TO 700
700 CONTINUE
SORT
NOSORT
END
STOP

SUBROUTINE CAT(Z,FF,DERF,TM1,TM2,TD1,CD;TD2,CEC,ALPH2,BETA2,
1TM3,TT1,SIGMA,ALPH3)
* SUBROUTINE CAT FOR CALCULATION OF CATION EXCHANGE EQUATION AND
DERIVATIVE
* Z-RESULTANT ROOT OF EQUATION F(Z)
* FF RESULTANT FUNCTION ROOT OF EQUATION F(Z)
* DERF RESULTANT VALUE OF DERIVATIVE AT ROOT Z
* TM1-TOTAL AMOUNT MONOVALENT CATION1 SODIUM
* TM2-TOTAL MONOVALENT CATION2 POTASSIUM
* TM3- TOTAL MONOVALENT CATION3 HYDROGEN
* TD1 TOTAL AMOUNT OF DIVALENT CATION1 CA
* TD2 TOTAL DIVALENT CATION2 MG
* TT1- TOTAL TRIVALENT CATION1 ALUMINIUM
* CEC = SUM AM(I)+AD(I)+AT(I)
* CD=KD1/KM1
* ALPH2=KM1/KM2

```

```

*      ALPH3=KM1/KM3
*      BETA2=KD1/KD2
*      SIGMA=KT1/KD1
*      C
*
      F1=TM1/(1.+Z)
      F2=TM2/C1.+ALPH2xZ)
      F3=TM3/(1.+ALPH3xZ)
      F4=TD1/(1.+CDxZxZ)
      F5=TD2/C1.+BETA2xCDxZxZ)
      F6=TT1/(1.+SIGMAxZxZxZ)
      FF=F1+F2+F3+F4+F5+F6-CEC
      DERF1=TM1/(1.+Z)xx2
      DERF2=ALPH2xTM2/(1.+ALPH2xZ)xx2
      DERF3=ALPH3xTM3/(1.+ALPH3xZ)xx2
      DERF4=TD1xCDxZx2./(1.+CDxZxZ)xx2
      DERF5=TD2xCDxZx2.xBETA2/(1.+CDxZxZxBETA2)xx2
      DERF6=3xZxZxTT1xSIGMA/(1.+SIGMAxZxZxZ)xx2
      DERF=-1.x(DERF1+DERF2+DERF3+DERF4+DERF5+DERF6)
      RETURN
      END
*
*
*      RTNI SUBROUTINE.NEWTON ITERATION METHOD
*
*
      SUBROUTINE RTNI(FF,DERF,XST,EPS,IEND,TM1,TM2,ID1,CD,TD2,
1  CEC,ALPH2,BETA2,TM3,TT1,SIGMA,ALPH3,X,IER,IK,IEPS)
*
*
*      X- RESULTANT ROOT OF EQUATION F(X)=0
*      FF- RESULTANT FUNCTION VALUE AT ROOT X
*      DERF- RESULTANT VALUE OF DERIVATIVE AT ROOT X
*      XST -INITIAL VALUE OF X FOR ITERATION
*      FPS- UPPERBOUND OF ERROR OF RESULT X
*      IEND- MAXIMUM NUMBER OF ITERATION STEP SPECIFIED

```

```

*      IER=0-NO ERROR
*      IER=1-NO CONVERGENCE AFTER IEND STEP
*      IER=2-DERF EQUAL TO ZERO AT SOME ITERATION STEPS
*      IER=3-AT SOME PLACE DX.GT.X WAS CORRECTED, MESSAGE ONLY
*      IER=4-AFTER CORRECTION DX RESTS.GT.X
*      IK-ITERATION COUNTER
*      PREPARATION ITERATION
      IEPS=0
21  IK=0
      IER=0
      X=XST
      TDL=X
      CALL CAT(TOL,FF,DERF,TM1,TM2,ID1,CD,TD2,CEC,ALPH2,BETA2,
        1TM3,TT1,SIGMA,ALPH3)
13  TOLF=100.*EPS
*
*      START ITERATION LOOP
*
      6  IK=IK+1
          IF(FF)1,7,1
*
*      EQUATION IS NOT SATISFIED BY X
      1  IF(DERF)2,8,2
*
*      ITERATION IS POSSIBLE
      2  DX=FF/DERF
*
*      CHECK FOR NEGATIVE X
14  IF(DX-X)17,15,15
15  DX=0.9*DX
      IF(IK-20)16,18,18
*      IER=3- AT SOME PLACE DX.GT.X WAS CORRECTED*****
16  IER=3
      GO TO 14
17  CONTINUE
      X=X-DX

```

```

TOL=X
CALL,CAT(TOL,FF,DERF, TM1, TM2, TD1, CD, TD2, CEC, ALPH2, BETA2,
1TM3, TT1, SIGMA, ALPH3)
CONTINUE

```

```

*

```

```

*   TEST ON SATISFACTORY ACCURACY*****

```

```

10 TOL=EPS
   A=ABS(X)
   IF(A-1.)4,4,3
   3 TOL=TOL*A
   4 IF(ABS(DX)-TOL)5,5,36
   5 IF(ABS(FF)-TOLF)7,7,36
36 IF(IK-IEND)6,6,26

```

```

*   END OF ITERATION LOOP

```

```

*

```

```

*   NO CONVERGENCE AFTER IEND STEPS

```

```

26 IER=1
   IF(IEPS-2)19,7,7

```

```

*

```

```

*   EPS IS INCREASED BY FACTOR TEN

```

```

19 IEPS=IEPS+1
   EPS=EPS*10.

```

```

*   BACK TO ITERATION CYCLE WITH NEW EPS

```

```

   TOLF = 100.*EPS
   GO TO 10

```

```

7 RETURN

```

```

*   ERROR RETURN IN CASE OF ZERO DIVISION

```

```

8 IER=2
   RETURN

```

```

*   C

```

```

*   ERROR RETURN FOR DX.GT.X,CORRECTION NOT EFFECTIVE

```

```

18 IER=4
   RETURN
   END

```

Appendix 6.2 List of acronyms used in the program

Acronym	Definition	Units
AALI	initial amount of aluminium	(eq)
ACAI	initial amount of calcium	(eq)
ACOND	average conductivity	(m.d ⁻¹)
AHYDI	initial amount of hydrogen	(eq)
AKI	initial amount of potassium	(eq)
ALI	initial exchangeable aluminium	(eq.m ⁻³)
AMGI	initial amount of magnesium	(eq)
AMOX	amount of oxygen	(kg)
AMOXI	initial amount of oxygen	(kg)
AMW	amount of water	(m ³)
AMWI	initial amount of water	(m ³)
ANAI	initial amount of sodium	(eq)
APDIFA	apparent diffusion coefficient of aluminium	(m.d. ⁻¹)
APDIFC	apparent diffusion coefficient of calcium	(m.d. ⁻¹)
APDIFH	apparent diffusion coefficient of hydrogen	(m.d. ⁻¹)
APDIFK	apparent diffusion coefficient of potassium	(m.d. ⁻¹)
APDIFM	apparent diffusion coefficient of magnesium	(m.d. ⁻¹)
APDIFN	apparent diffusion coefficient of sodium	(m.d. ⁻¹)
CAI	initial exchangeable calcium	(eq.m ⁻³)
CALI	initial concentration of aluminium in soil solution	(eq.m ⁻³)
CCAI	initial concentration of calcium in soil solution	(eq.m ⁻³)
CEC	cation exchange capacity	(eq.m ⁻²)
CHYDI	initial concentration of hydrogen in soil solution	(eq.m ⁻³)
CKI	initial concentration of potassium in soil solution	(eq.m ⁻³)
CMGI	initial concentration of magnesium in soil solution	(eq.m ⁻³)
CNAI	initial concentration of sodium in soil solution	(eq.m ⁻³)

Acronym	Definition	Units
COND	hydraulic conductivity	$(\text{m} \cdot \text{d}^{-1})$
CONSAT	saturated hydraulic conductivity	$(\text{m} \cdot \text{d}^{-1})$
COX	concentration of oxygen	$(\text{kg} \cdot \text{m}^{-3})$
COXI	initial concentration of oxygen	$(\text{kg} \cdot \text{m}^{-3})$
CSO ₄	concentration of sulphate	$(\text{eq} \cdot \text{m}^{-3})$
CSO ₄ I	initial sulphate concentration	$(\text{eq} \cdot \text{m}^{-3})$
DEF	effective diffusion coefficient	$(\text{m}^2 \cdot \text{d}^{-1})$
DEFAC	diffusion efficiency factor	(unitless)
DEPTH	distance from the middle of a compartment to the soil surface	(m)
DEVAP	evaporation rate from soil surface	$(\text{m} \cdot \text{d}^{-1})$
DFLAL	rate of diffusion of aluminium	$(\text{eq} \cdot \text{m}^{-2} \cdot \text{d}^{-1})$
DFLCA	rate of diffusion of calcium	$(\text{eq} \cdot \text{m}^{-2} \cdot \text{d}^{-1})$
DFLH	rate of diffusion of hydrogen	$(\text{eq} \cdot \text{m}^{-2} \cdot \text{d}^{-1})$
DFLK	rate of diffusion of potassium	$(\text{eq} \cdot \text{m}^{-2} \cdot \text{d}^{-1})$
DFIMG	rate of diffusion of magnesium	$(\text{eq} \cdot \text{m}^{-2} \cdot \text{d}^{-1})$
DFLNA	rate of diffusion of sodium	$(\text{eq} \cdot \text{m}^{-2} \cdot \text{d}^{-1})$
DFLOX	rate of oxygen diffusion	$(\text{kg} \cdot \text{m}^{-2} \cdot \text{d}^{-1})$
DFLSO	rate of diffusion of sulphate	$(\text{eq} \cdot \text{m}^{-2} \cdot \text{d}^{-1})$
DIFD	distance between the centres of two adjacent compartments	(m)
DISP	dispersion factor	(m)
DNOTH	diffusion coefficient of hydrogen	$(\text{m}^2 \cdot \text{d}^{-1})$
DNOTAL	diffusion coefficient of aluminium	$(\text{m}^2 \cdot \text{d}^{-1})$
DNOTCA	diffusion coefficient of calcium	$(\text{m}^2 \cdot \text{d}^{-1})$
DNOTK	diffusion coefficient of potassium	$(\text{m}^2 \cdot \text{d}^{-1})$
DNOTMG	diffusion coefficient of magnesium	$(\text{m}^2 \cdot \text{d}^{-1})$
DNOTNA	diffusion coefficient of sodium	$(\text{m}^2 \cdot \text{d}^{-1})$
DPGWT	depth of groundwater table	(m)
DZERO	diffusion coefficient of oxygen in air	$(\text{m}^2 \cdot \text{d}^{-1})$
HI	initial exchangeable hydrogen	$(\text{eq} \cdot \text{m}^{-3})$
IPSI	initial hydraulic potential	(m)
ITCOM	initial thickness of compartment	(m)

Acronym	Definition	Units
KI	initial exchangeable potassium	(eq.m^{-3})
MFLAC	rate of mass flow of calcium	$(\text{eq.m}^{-2}.\text{d}^{-1})$
MFLAL	rate of mass flow of aluminium	$(\text{eq.m}^{-2}.\text{d}^{-1})$
MFLH	rate of mass flow of hydrogen	$(\text{eq.m}^{-2}.\text{d}^{-1})$
MFLK	rate of mass flow of potassium	$(\text{eq.m}^{-2}.\text{d}^{-1})$
MFLMG	rate of mass flow of magnesium	$(\text{eq.m}^{-2}.\text{d}^{-1})$
MFLNA	rate of mass flow of sodium	$(\text{eq.m}^{-2}.\text{d}^{-1})$
MFLOX	rate of oxygen mass flow	$(\text{kg.m}^{-2}.\text{d}^{-1})$
MFLSO	rate of mass flow of sulphate	$(\text{eq.m}^{-2}.\text{d}^{-1})$
MGI	initial exchangeable magnesium	(eq.m^{-3})
NAI	initial exchangeable sodium	(eq.m^{-3})
NFLAL	net flow rate of aluminium	$(\text{eq.m}^{-2}.\text{d}^{-1})$
NFLCA	net flow rate of calcium	$(\text{eq.m}^{-2}.\text{d}^{-1})$
NFLHYD	net flow rate of hydrogen	$(\text{eq.m}^{-2}.\text{d}^{-1})$
NFLK	net flow rate of potassium	$(\text{eq.m}^{-2}.\text{d}^{-1})$
NFLMG	net flow rate of magnesium	$(\text{eq.m}^{-2}.\text{d}^{-1})$
NFLNA	net flow rate of sodium	$(\text{eq.m}^{-2}.\text{d}^{-1})$
NFLOX	net flow rate of oxygen	$(\text{kg.m}^{-2}.\text{d}^{-1})$
NFLSO	net flow rate of sulphate	$(\text{eq.m}^{-2}.\text{d}^{-1})$
NFLW	net flow rate of water	$(\text{m}.\text{d}^{-1})$
PSI	hydraulic potential	(m)
PSO ₄	rate of sulphate production	$(\text{kg.m}^{-3}.\text{d}^{-1})$
PVOL	pore volume	$(\text{m}^3.\text{m}^{-3})$
PYR	depth of pyritic layer	(m)
RCOX	rate of oxygen consumption	$(\text{m}^{-3}.\text{m}^{-2}.\text{d}^{-1})$
REDFDT	reduction factor for actual evaporation	(unitless)
RFLOW	flow rate of water	$(\text{m}.\text{d}^{-1})$
RHYD	rate of production of hydrogen	$(\text{eq.m}^{-2}.\text{d}^{-1})$
SUCT	matric suction	(m)
TALI	total amount of aluminium	(eq)
TCAI	total amount of calcium	(eq)
TCOM	thickness of compartment	(m)
TD	total divalent cations	(eq)

Acronym	Definition	Units
THYDI	total amount of hydrogen	(eq)
TKI	total amount of potassium	(eq)
TM	total monovalent cations	(eq)
TMGI	total amount of magnesium	(eq)
TNAI	total amount of sodium	(eq)
TT	total trivalent cations	(eq)
WC	water content	(m ³ m ⁻³)
WCFC	water content at field capacity	(m ³ m ⁻³)
WCI	initial water content	(m ³ m ⁻³)
WCLIM	water content at wilting point	(m ³ m ⁻³)

In potential acid sulphate soils acidity may arise from any combination of reclamation and drainage lowering the groundwater table in adjacent areas, and unusually dry seasons affecting the regional groundwater table. In the long run, natural processes of deacidification will finally make these soils productive. But this natural process is very slow and may take decades for any significant improvement. Thus natural reclamation does not provide the solution to the immediate need of increasing food production at a sufficiently high rate. Developing economic means of enhancing the process of reclamation of these soils is therefore considered very important. Feasible management packages for the development of acid sulphate soils are determined by the soils, the climate, the hydrology and the economic opportunities.

The causes of low productivity of acid sulphate soils include soil acidity, salinity, aluminium toxicity, iron toxicity and low nutrient status. Different reclamation and improvement methods for low land rice are reviewed in Chapter 2. A simple low-cost lysimeter drum (60 cm diameter, 90 cm depth) was developed to collect undisturbed soil cores for studying the chemical changes and the growth of rice in acid sulphate soils. Forty undisturbed soil cores from Aparri and Sinacaban soils in the Philippines were subjected to different water management practices, liming rates and mulch application for two leaching periods and three rice crops. There was a great difference in chemical properties and grain yields of the two soils. In Aparri soil, there was no marked effect of drainage, liming and mulch practices on the chemical properties of the soil solution during the two leaching periods and

during three rice crops. Also the grain yields of three crops in this soil were not influenced by different treatments.

In Sinacaban soil, the effects of drainage, liming and agronomic practices on chemical properties of soil solutions were very pronounced. Deep drainage of the soil created favourable conditions for pyrite oxidation which resulted in high acidity and high Fe^{2+} and Al^{3+} . Shallow drainage did not cause severe oxidation in the subsoil layers and produced less acidity and Fe^{2+} , Al^{3+} . Shallow drainage in combination with mulch application (5 cm of rice straw) minimized the water loss from the soil, and hindered oxygen movement to the subsoil. This resulted in less acidity development and less Fe^{2+} , Al^{3+} . When the soil was continuously submerged, there was no pyrite oxidation, and no Fe^{2+} and Al^{3+} production.

The influence of different treatments on grain yields was very pronounced. Deep drainage treatments gave the poorest yield in both the second and third crops. Highest yields were obtained in the surface flushing treatments, the next highest yields with shallow drainage. Mulching increased grain yield by 67 and 30 percent for the second and third crops respectively. In deep drainage treatments, only high amounts of lime, 2.5 tons/ha produced a yield exceeding the equivalent of about 1 ton/ha. In this chapter, the concept of average mineral stress index (AMSI) was introduced to correlate grain yield and toxic elements in acid sulphate soils (pH, Al, Fe).

During the dry season, oxidation and acidification occur when groundwater falls below the sulphic layers in the subsoil.

In Chapter 3, a study on the evaporation and acidification process in an acid sulphate soil was carried out in fourteen undisturbed soil columns of 20 cm in diameter and 70 cm length from an acid sulphate soil in Mijdrecht, the Netherlands. These columns were subjected to two groundwater levels: 40 cm and 65 cm below the soil surface, 5 different durations of evaporation and 2 agronomic practices. The average total acidity over 14 layers in the profile did not show much variation among treatments. The presence of a peat layer on the surface reduced the rate of acidification, presumably mainly by reducing. The evaporation rate and perhaps by hampering the oxygen movement in the profile. In treatments with low groundwater table, the average pH decreased sharply

at increasing evaporation.

When acid sulphate soils develop, dramatic changes in the chemistry of surface waters take place and these are exported from the reclaimed area as drainage waters. Acid sulphate floodwaters generated over large areas of acid sulphate soils may adversely affect crops growing on adjacent, better soils.

In Chapter 4, a study on the one-time and cumulative effects of acid sulphate floodwater on the growth of rice and on the chemical changes in three acid sulphate soils were investigated in two successive pot experiments. Artificial acid floodwater were made with pH ranges from 3.5 to 5.8, Al^{3+} from 0 to 300 mg/l and Fe^{2+} from 0 to 500 mg/l.

In both experiments, pH of acid floodwater alone, as low as 3.5, did not affect the chemical changes of three acid sulphate soils, whereas the presence of Al^{3+} and Fe^{2+} in acid sulphate floodwater produced low pH and enhanced the solubility of Fe^{2+} .

pH of acid sulphate floodwater alone as low as 3.5 showed no effect of the growth of rice at an early stage of growth. Dry matter yields were negatively correlated with the applied Fe^{2+} and Al^{3+} .

A single factor, total acidity, being the sum of H^+ , Al^{3+} and Fe^{2+} in equivalents, was introduced as a factor determining the plant dry matter yield in cases that none of these reached the limiting toxicity values.

In acid sulphate soils, rice responded favourably to rock phosphates. Phosphorus is the main limiting macro-nutrient for crop production in these soils, but the use of superphosphate is a luxury in many developing countries because of their limiting foreign exchange. Therefore, the effectiveness of rock phosphates for lowland rice on acid sulphate soils under various management practices was studied in pot experiments on surface horizons of two acid sulphate soils under three application methods and two rates. Details of this experiment is given in Chapter 5. Rice response to phosphate sources varied between soil. In Malinao, the highest rice yield was obtained when rock phosphate was applied and incubated three weeks before transplanting at field capacity.

In Chapter 6 a computer simulation model was developed to calculate the time course of acidity production from pyrite oxidation in relation to the changes of groundwater table, evaporation, entrance of oxygen and different chemical reactions. The model is based on a multicompartment model in which the soil profile is divided into a number of layers, is written in CSMP and contains three main parts: INITIAL, DYNAMIC and TERMINAL. For each compartment of a clay loam and a silty clay soil, the compartment thickness, its water content, pyrite content, cation exchange capacity, total cations, adsorbed cations and oxygen concentration are given as inputs. Three evaporative demands of 4, 6 and 9 mm.d^{-1} were used as a boundary condition at the soil surface. These substantial differences in evaporative demand lead to increasing water-loss. Results show that the oxidation process and the associated acidification of the soil are only marginally affected by the different evaporative demands, although the oxidation rate was very much influenced during the early part of the evaporation process.

Results from this thesis shows that minimizing the oxidation of pyrite by application of mulch during the dry season and maintaining higher groundwater tables can avoid the acidic hazards. Research along this line should be directed toward the feasible application of this package to the field. In addition, other experiments should be carried out to study the following:

- varietal screening for short duration, acid-tolerant, salt-tolerant, iron-tolerant cultivars;
- studies on fertilizer application should aim at optimizing the use of phosphate, preferably rock phosphate;
- development of quantitative models to predict the effects of drainage at various depths, irrigation and other management practices on the physical and chemical properties of acid sulphate soils.

In order to validate these models, basis data on physical and chemical processes under various boundary conditions are needed.

CURRICULUM VITAE

The author was born in January 10, 1951 in Quang Nam, Da nang Province, Viet Nam. He finished his high school in 1969 and graduated at the National Agricultural Institute, Saigon as Agricultural Engineer (major in Irrigation and Drainage) in 1973. Soon after his graduation, he obtained a fellowship to persue further study at the University of the Philippines at Los Baños. He gained a M.Sc. degree in Agricultural Engineering (major in Irrigation and Drainage and minor in Soil Sciences). In 1977 the author was sponsored by The Interim Mekong Committee, the International Rice Research Institute and the Dutch technical cooperation program to carry out his promotion work for the degree of Doctor of Agricultural Sciences at Wageningen Agricultural University.