

FACTORS AFFECTING FERTILITY OF
SELECTED BROWN SAND SOILS
OF GUYANA

By

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A Dissertation Presented to the Graduate Council of
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in Partial Fulfillment of the Requirements for the
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. . . to those
for whose interest and guidance
my expressions of gratitude can
never be truly adequate . . .

Mrs. Irene A. Wilson

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Alfred Victor Downer

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Chairman: Dr. W. G. Blue

Major Department: Soil Science

Samples of four soils of the "white sand" plateau of Guyana were used in an effort to delineate fertility characteristics and describe means of improving crop production levels.

Laboratory studies indicated that kaolinite was the clay mineral in all the soils but that its contribution to cation exchange capacity was negligible; more than 90 per cent of the cation exchange sites were supplied by the organic fraction. Exchangeable bases were low in all soils, and K and Mg were increasingly leached from the soils as pH increased. The three brown sand soils - Tabela sand, Kasarama loamy sand, and Ebini sandy loam - differed as a group from the Tiwiwid sand. The former soils were relatively rich in amorphous material with fulvic acids dominant in the organic fraction while the latter soil was poorly supplied with amorphous material and its organic fraction was dominated by humic acids. The Tiwiwid sand had a lower pH but a larger supply of plant nutrients than the brown sand soils.

Substantial amounts of P were extractable from the Tiwiwid sand, and virtually all added P was recoverable by the Bray #1 extractant. The brown sand soils had very small amounts of P and less than 70 per cent of added P was recoverable.

Plant growth under controlled moisture was better on the Tiwiwid sand than on the brown sand soils, with N appearing to be the nutrient which evoked the largest response. On the latter soils, P appeared to limit plant growth but positive responses to added micronutrients were also obtained.

Pigeon pea responded positively to lime on the Tiwiwid sand, but pangolagrass yields were depressed by lime on the brown sand soils. This negative response was apparently due to fixation of P at higher pH levels, as fulvate ions of fulvate-Al complexes were replaced by P.

Practices aimed at the improvement of the level of fertility in these soils must minimize the loss of nutrients by leaching. The use of lime on the brown sand soils will need to be carefully considered in relation to crop requirements and soil conservation.

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INTRODUCTION

"The soil comes first. It is the basis, the foundation of farming; without it, nothing; with poor soil, poor living; with good soil, good farming and living. An understanding of good farming begins with an understanding of the soil."

At first glance, the above statement made by Ahlgreen (3. p. 425) might seem to be a trifle platitudinous. Given some thought, however, it amounts to an effective summary of the rationale behind the major portion of man's endeavours on this planet. The statement can be construed as an immediate basis for the broad division of the world's surface into developed areas--the soil is understood to a considerable degree--and underdeveloped areas--the soil is understood only to a limited degree or not at all. If considered in conjunction with the Malthusian or "Dismal Theory" and available evidence on the relative rates of population growth and increase in food production, the statement makes an overwhelming case for the need to understand the soil.

In the so-called underdeveloped regions of the world, there are greatly overpopulated areas at one extreme and vast areas of uninhabited and unutilized land at the other extreme. The Amazon area lies at the latter extreme. This area supports vast stretches of apparently lush evergreen forests, but makes little or no contribution to the production of food or fiber.

Guyana falls largely within the phytogeographical unit comprised essentially of the Amazon basin (283), and though it has been the source of several agricultural products for some 400 years its soils are clearly not understood to any appreciable degree. About 8.5% of the land area of Guyana is composed of coastal sediments, and it is this area which has supported the major part of the population and provided the bulk of the agricultural production throughout its existence. Soils found on the remainder of the land area of Guyana, whether formed from in-situ weathering of Precambrian parent material or from transported material from similar sources, have been relatively unused. Extensive systems of cattle rearing have been practised on areas of the non-coastal soils since the latter half of the nineteenth century with varying degrees of success. While production in the Rupununi has been maintained at relatively low levels of efficiency, all early efforts in the Ebini area failed completely. Several studies have been undertaken to delineate the reasons for early failures, but complete understanding of the phenomena which determine the level of fertility of soils at Ebini has still to be achieved. This has encouraged neither the modification of methods of production nor the increase in productivity of these soils, and the non-coastal soils of Guyana have remained virtually unused. However, data compiled by the F. A. O. Soil Survey project and published in 1965 indicated the potential value of the Ebini area as a launching site for the development of a viable agricultural program based on the utilization of non-coastal soils. Accordingly, four soil types were selected from the Ebini area for study. The immediate objectives being:

- (a) delineation of the fertility characteristics of the soils.
- (b) description of possible methods of optimizing or ameliorating crop production levels.

The extremely low level of inherent fertility and the free leaching to which Wagenaar (315) found the soils to be subject suggested that the objectives might best be realized by an examination of characteristics which influence the retention of added nutrients. This examination could then be supplemented by greenhouse studies aimed at establishing the optimal levels of some of the major nutrients which could be beneficially applied to the soils.

Fangolagrass (Digitaria decumbens Stent) and pigeon pea (Cajanus cajan (L) Druce) were used as indicator crops. Selection of a grass and a legume for these purposes was influenced by the idea that the ultimate system of agriculture would most likely revolve around pastures. Cattle would provide a means of recycling nutrients, and grass or grass-legume associations a means of maintaining desirable levels of organic matter in the soil.

REVIEW OF LITERATURE

Guyana

Guyana covers an area of about 225,000 km² extending from 1° 10' N to 8° 35' N, and from 56° 38' W to 61° 28' W. Its narrow coastline extends along the Atlantic coast of South America from just west of the Orinoco Delta to the Corentyne River. Deposition of suspended material borne by the numerous rivers within Guyana, and by the Amazon, has produced a thin strip of "coastal soils," but by far the greater portion of the country is made up of material from the Guiana Shield. The non-coastal soils have not been very widely used for agricultural production, but interest in their utilization is increasing steadily.

Ebini Area

Location

Ebini is situated at about 5° 40' N and 57° 40' W in the north-eastern portion of Guyana. It lies within the area of the Berbice savannas (251) which because of their position, relative to the coastal land and to the Rupununi savannas, are known colloquially as the "Intermediate Savannas."

Climate

Wagenaar (315) summarized available data on the climate of the Ebini area. He stated that the climate, broadly categorized as

equatorial, could be subclassed as a "tropical rainforest climate, continuously moist."

Mean annual temperature (for 1962 only) was 26.9°C with the highest monthly mean--28.2°C--in October, and the lowest--25.5°C--in January. The absolute minimum temperature in that year was 17.8°C, recorded in September-October.

Day-length was thought to vary by less than 22.5 min. from the mean of 12 hours 7.5 min. recorded in Georgetown.

The mean annual rainfall is approximately 2,200mm with a recorded minimum of 1,550mm and maximum of 3,435mm. The pattern of rainfall distribution was described as:

A long rainy season (mid April to mid August).

A long dry season (mid August to late November).

A short rainy season (late November to early February).

A short dry season (early February to mid April).

The long rainy season accounts for about 50% of the average annual rainfall.

He estimated that the annual evaporation was about 127cm, and suggested that because of its unreliability, rainfall was probably the most important climatic factor in agriculture in the Ebini area (315).

Vegetation

Sombroek (283) argued that the Guianas fall within the northern boundary of the phytogeographical unit of Amazonia, and this is supported by Vann (303) who reported a marked similarity in vegetation across the Guianas. Richards (251) indicated that the savannas in

Surinam are very much like the Berbice savannas. These areas are dominated by grasses with "islands" of bushes and trees as well as strips of fringing forests located in stream valleys. The most common grass species is Trachypogon plumosus, with admixtures of Axonopus aureus, Axonopus strigatus, and Andropogon virginicus. The most common trees are Curatella americana and Byrsonima crassifolia (45).

Physiography

The Ebini area lies within the northern regions of the physiographic unit designated as the "white sand" plateau. This plateau is of a somewhat uniform monotonous topography with gently undulating relief. It rises from an elevation of about 16m in the north to about 160m in the south. Its surface is dominated by irregularly distributed areas of white quartz sand (white sand) and brown loamy sand to sandy clay (brown sand). These sands are thought to have developed from sediments deposited by rivers flowing from the upper Rio Branco Basin, and Vann (303) concluded that the time deposition was approximately 227,000 years ago during the third interglacial period. Bleackley and Khan (32) stated that the white sand plateau constitutes part of a soil formation which covers a wedge-shaped area of some $45,000 \text{ km}^2$ in Guyana, Surinam, and French Guiana. Within Guyana the white sand plateau extends over about $26,000 \text{ km}^2$ and of this the brown sands occupy approximately $9,000 \text{ km}^2$. Most of the brown sands support forest; only about 770 km^2 support savannas. They reported that the white sands occupy the topographically highest point in a given locality within the confines of the plateau as well as areas sloping towards waterways.

Richards (251) observed that the soils of the Berbice savannas are mainly brown sands but these change to bleached sands with changes in vegetation.

Geology

Hardy and Follett-Smith (119) estimated that the non-marine sediments in Guyana were derived initially from an Archaean gneiss granite basement complex associated with a volcanic series. The Geological Survey Department of Guyana lists several stratigraphic units, and among these is a group of Tertiary to Pleistocene and Holocene continental-deltaic sediments--the Corentyne group. The white sand plateau which seems to be identical to the Berbice formation forms part of the Corentyne group of sediments.

Soils

The soils of the white sand plateau include regosols, red-yellow latosols, red-yellow podzols, and ground water laterites displaying various phases and degrees of intergrading. Red-yellow latosols and regosols are the dominant soils. Brinkman (45) reported the occurrence of at least 15 soil types in the intermediate savannas. The soils of most extensive occurrence include the Kasarama loamy sand (56,600 ha), Tiwiwid sand (40,480 ha), Tabela sand (27,640 ha), and Ebini sandy loam (26,300 ha). An apparent characteristic of the area is the occurrence of "black water" streams, the coloration of which is thought to be due to the movement of organic matter down the soil profile and into the drainage system.

Soil Utilization

Richards (251) cited burning and grazing practices as factors which may have influenced the development of vegetation in the Berbice savannas. This would suggest that shifting cultivation may have been the practice on these soils at some time, but no data are now available to establish or refute this. Inaccessibility of relevant records, at this time, also precludes any meaningful discussion or interpretation of the effects of settlements in the area during the seventeenth and eighteenth centuries.

According to Mayers (186), introduction of cattle to the Rupununi savannas in the 1850s, or thereabouts, led to the utilization of the Berbice savannas for the grazing and resting of animals being driven to market. Subsequently efforts at more long-term utilization of these savannas revealed that the prolonged grazing of cattle resulted in infertility and frequently in death of the animals. Solutions to this problem were actively sought and in 1941 the Ebini Livestock Station was established with the primary objective of facilitating the development of extensive systems of beef production. This objective was modified in 1957 to include the solution of problems likely to occur in intensive systems of production. Exploratory studies on pasture grasses and grass/legume associations were initiated, and later field crop studies were commenced (186). More recently, there has been some crop production in the area, but the extent of utilization of the Berbice savannas remains limited.

Brown Sands

The term "brown sands" has been in use for some time as a broad description of the soils of the Berbice savannas. The broad grouping permits comparisons with those portions of the white sand plateau which extend into Surinam--the Zanderij formation--, and French Guiana--Sols Ferralliques typiques--. However, the description of soils on an individual basis is to be preferred since this provides the opportunity for comparison with similarly developed profiles in other parts of the world. Such comparisons are necessary if only because of the very limited amount of analytic data published about the brown sands.

From individual profile descriptions, the brown sand soils are seen to be in fact predominantly red-yellow soils. The Tiwiwid sand appears to be an exception, but Bleackley and Khan (31) reported that humic B horizons of up to 30cm in thickness or reddish horizons (32) were found at depths of less than 12m from the surface of this soil. They described lateral transitions from white sand through pale yellow sands to red sandy loams, and noted that the boundaries of the bleached sands tended to coincide with the presence of humic layers. They also noted that the pans of precipitated Fe and humic matter were to be found at about the level of the water table (31). Comparable findings were reported by Andriesse (14) for red-yellow soil associations in Sarawak.

Richards (251) described the Tiwiwid sand as a "lowland tropical podzol" and compared it to the "Padang" soils of Borneo described by Hardon. He suggested that the bleached sands were the products of degradation of less sandy soils, and attributed the degradation to

the effects of organic materials which were not precipitated because of the low base status of the soils. There is, however, some controversy as to the true parent material of the Tiwiwid sand. It would appear that there are three possible sources of parent material. The first possibility is brown sandy soils as proposed by Richards (251), and supported by the data adduced by Bleackley and Khan (31, 32). The second possibility is sand dunes or other coastal deposits, and this is supported by the occurrence of a series of bauxite deposits along the southern extremities of the white sand plateau in Guyana and Surinam. These deposits coincide roughly with the coastline of South America prior to the first interglacial period, but Vann (303) argued against the possibility of parent material of marine origin. He listed several reasons among which were the lack of "ridges" or other shoreline features, the absence of shell remains, and the close similarity to mineral assemblages of inland rocks. The third possibility is based on a conclusion arrived at by Klinge (157). He observed a catena-like relationship between white sand regosols and red-yellow soils in the Manaus area of Brazil, and concluded that both of the sources indicated above may have contributed to the parent material from which bleached sands developed.

Despite the lack of a characteristic red-yellow coloration, there may be some genetic relationships to the brown soils proper--the Tabela sand, the Kasarama loamy sand, and the Ebini sandy loam. These relationships can be appreciated in light of available data on the role of organic materials in the alteration of soils. Andriesse (14) distinguished between elaphic podzols in Sarawak, the formation of which is

dependent on the porous nature of the parent material, and the climatic podzols of the temperate zone which have their origin in the surface accumulation of organic residues. Though such a clear distinction is unrealistic in this case, the effects of percolating water cannot be ignored. Kemper (150) attested to the disruptive effect on soil aggregates of moving water and the abrasive action of solid particles suspended in it. Thorp *et al.* (298) related the porosity of the soil to the movement of bases, sesquioxides, clay particles, and clay particle constituents. The solvent effect of dissolved materials has been reported by various workers. Bloomfield (33) found differences in the degree of dispersion of soil particles caused by polyphenols, and established that the polyphenols could mobilize ferric oxides as ferrous complexes of considerable stability. Davies *et al.* (71) characterized the Fe-polyphenol compounds as easily transported non-ionic complexes. Malcolm and McCracken (180) categorized the effects of canopy drip from different plant species in terms of pH, polyphenol composition, and capacity for complexation of Al and Fe. They determined that polyphenols, reducing sugars, and organic acids were the principal agents of Fe mobilization, but that lower concentrations of dissolved material enhanced mobilization. Their suggestion that the Ca^{2+} status of the soil had no effect on the mobilization of Al and Fe differed from that of DeLong and Schnitzer (75) who reported that Ca^{2+} greatly decreased the solubility in water of Fe-organic matter complexes. The importance of hydroxy-acids, e.g., tannic acid, in the mobilization of Fe and the strong coloration of drainage water (298) lends support to the argument advanced by Richards (251). He proposed that the high

tannin content of the residues of the legumes, e.g., *Eperua* spp., supported by the Tiwiwid sand was largely responsible for degradation of brown sandy soils, and development of the Tiwiwid profile.

Both parent material and climate will have influenced the nature and composition of the soil mass. Bennema (26) indicated that under conditions of high temperature and rainfall, red-yellow latosols with transitions to regosols and red-yellow podzols are the soils likely to be formed. Such soils characteristically have an inorganic portion comprised of small amounts of silt, 1:1 silicate clays, sesquioxides (usually less than 10% (W/W) of the clay fraction), and larger quantities of quartz or other minerals which are highly resistant to weathering (26). The climatic conditions encourage intense oxidation of organic substances, but low pH and moist conditions inhibit condensation of the decomposition products, thereby permitting appreciable quantities of low molecular-weight compounds to exist in the organic fraction (159).

The properties of any soil arise from the composition of the soil mass. Structurally, red-yellow soils display fine granules adhering closely to each other to produce a friable mass (26). They are physically very suitable for plant growth, as indicated by Ignatieff and Lemos (136), but are usually very poorly supplied with plant nutrients. They have low cation exchange capacities, and relatively large capacities for anion sorption and phosphate fixation. Sombroek (283) provided detailed description of the chemical properties and nutrient status of several red-yellow soils in the Amazon basin.

Fertility Concepts Concerning the Red-yellow
Soils of the Tropics

The concept of a fertile soil refers to the capacity of the soil to supply nutrients in adequate quantities to growing plants as required. This implies that the soil has either a store of nutrients in the form of weatherable minerals of appropriate composition or that it has the capacity to retain adequate quantities of any nutrients added to that soil. The mode of formation of the red-yellow soils of the tropics and the characteristic composition of the soil mass imply that readily weatherable minerals which can supply nutrient elements required for plant growth are absent or virtually so. The level of fertility encountered in these soils, therefore, is dependent on the store of nutrients which is or could be held against leaching in forms available to plants. Such stores of nutrients are generally extremely low.

Despite their low nutrient status many red-yellow soils support lush evergreen forests. This anomaly has been explained by Nye and Greenland (221) in terms of nutrient cycling. Vegetation plays a vital role in the storage of nutrients which are returned to the soil in organic form as litter, rainwash, and root excretions (219). Mineralization of these materials provides inorganic ions for plant uptake. The theory was also applied to savannas. Grasses were found to contain, prior to leaf fall, almost the entire nutrient reserve in the system (221). This is essentially a closed cycle, and differs only in the mineralization phase from the "direct nutrient cycle" proposed by Went and Starke (321). Their theory involved endotrophic mycorrhizae with fungal hyphae providing continuous conduits from litter to root

and leaving little or no inorganic nutrients to be lost by leaching. Both mechanisms provide an explanation for the rapid loss of fertility seen on the cultivation of highly weathered tropical soils. Not only are exchangeable and mineralized nutrients lost, but soluble products of decomposing organic material move down the profile selectively removing ions from the soil mass. Large amounts of Ca, Mg, and F and traces of K and Fe have been mobilized by non-hydroxy organic acids, while hydroxy-acids removed more Fe, less Ca, Mg, and K, and still less P (298).

Jones (143) alluded to a cycle of fertility within the soil profile, which embraced changes in soil structure and nutrient status, consequent upon the destruction of organic matter, as well as the movement of nutrients down the profile during periods of cultivation. The nutrients which penetrate to lower horizons are returned to the surface during fallow periods. This is in effect an open cycle and probably constitutes the philosophy of shifting cultivation. It does not provide, however, any information as to the relative quantities of the nutrients which are or can be retrieved.

Simonson (277) regarded the initially low base status concomitant with the prolonged weathering and leaching of ultisols as the key to sustained crop production under systems of simple technology, but it is apparent that the potential effect of the current leaching regime must be listed as a factor of basic importance. Its significance will be enhanced by the high infiltration rates (179) and low water holding capacities (225) of these soils. Effects of the leaching regime are appreciated through the changes induced in the natural vegetation

by progressive loss of nutrients. The litter produced changes to materials of lower base status and wider C/N ratios (14), reducing the richness of the closed nutrient cycle (89). Fungi instead of bacteria become the principal agents of decomposition in accordance with the changed microclimate as more highly acid organic residues accumulate (89). Nye and Greenland (221) observed that the nutrient level of the soil solution is dictated by the anion concentration. Walker (318) stated that though there might be an initial accumulation of P, N, and S in the organic fraction, these elements can be progressively reduced by leaching, and this culminates in reduction of N-fixation by colonizing legumes. Since the parent material is the only source of P in these soils, he concluded that P was the key element in pedogenesis and that its level in the soil at any point in time would place a ceiling on crop production.

The red-yellow soils of the tropics are generally accepted as being inherently infertile. Their utilization poses the problem of the preservation of fertility, and would appear to justify the definition of soil fertility as a function of the level of technological skills in, and available to, the farming population (37). Leaching and erosion need to be controlled, and cropping programs carefully considered. The initial level of fertility will reflect the balance between the movement of nutrients down the profile, and the root volume of the cultivated species. The rate of movement of nutrients within the soil will be determined by the effective capacity for nutrient retention, that is to say, by the nature of the adsorptive complex within the soil. Wagenaar (315) reviewed available data on the brown sand soils

of Guyana and reported from his studies on the Tabela sand and Kasarama loamy sand that fertilizers, applied over a period of years as well as during the period of his investigations, had caused no appreciable change in the nutrient status of the soils. Removal of bases and the consequent destruction of soil clays foster the development of acidity through increases in amounts of active Al in soils. This adds a further dimension to the fertility status of these soils. Problems of toxicity and reduction of exchange capacity by Al could possibly be encountered. Reeve and Sumner (248) suggested that the base retention properties of Natal Oxisols were influenced by the factors which determined the equilibrium position of the various forms of Al in the soil.

Adsorptive Complex

The adsorptive complex in any soil comprises the sum of the adsorptive properties of the charged constituents of the colloidal fraction of that soil. The functional characteristics of this fraction as measured by reaction, buffering capacity, base saturation, etc., are determined by the nature of the individual constituents, and the proportions of each in the total. The individual constituents may be organic or inorganic. Organic colloids are less thoroughly understood than inorganic colloids, but it is known that variations in composition and, therefore, in properties can occur among these colloids. They are, however, always entirely negatively charged or potentially so. Inorganic colloids may consist of various proportions of silicate clays and crystalline or amorphous hydrous oxides of Al and/or Fe. These

colloids may display negative or positive charges, or both.

In red-yellow tropical soils 2:1 silicate clays and allophanes are absent or nearly so. Pennema (26), and Ignatieff and Lemos (136) averred that the clay fraction of such soils consists essentially of kaolinite and sesquioxides. The contribution to the adsorptive properties of the soils attributable to the clay fraction is dependent on the degree of interaction between crystalline and the amorphous constituents. Superimposed upon this contribution, is that of the organic colloids, modified by interaction with the inorganic colloids. The mechanisms of interaction will thus determine the sum of the adsorptive properties of these soils and their susceptibility to change with changes in the conditions within the soil mass.

Inorganic Soil Colloids

Kaolinite

The structure and properties of kaolinite have been described by several workers (68, 112, 185). Schofield and Samson (266) showed that the kaolinite crystal could have both positive and negative charges at low pH levels. Increase in pH caused an increase in negative charges, and a decrease in positive charges up to an inflection point on the alkaline side of neutrality. They attributed the negative charges partially to dissociation of hydroxyl groups in the tetrahedral layer, acknowledging that such dissociation would be negligible in neutral and slightly acid conditions. An additional source of negative charges was thought to be isomorphous substitution in the tetrahedral layer. Fripiat (101) discussed this latter source of charge in terms of Al

in 4- rather than 6-coordination and suggested that the proportion of Al in 4-coordination and, therefore, the degree of isomorphous substitution would be determined by the pH at which clay synthesis occurred. At lower pH levels there is less Al in 4-coordination. Van Olphen (223) indicated that isomorphous substitution and other lattice imperfections would be relatively small in kaolinite. Charges on the clay particles would be due mainly to broken bonds on the edge of the crystals. Those charges due to isomorphous substitution would be negative, and exert a permanent effect manifest on the flat surfaces. Charges due to broken bonds would vary in nature with the pH of the medium and in the pH range in which they would be active. Broken bonds in the octahedral sheet would bear positive charges at low pH while those in the tetrahedral sheet would bear negative charges at high pH. The charges contributed by broken bonds thus exert a "pH-dependent" effect. The bulk of the charges on the kaolinite crystal were thought to be due to broken bonds (112), and their pH-dependent effect was diagrammatically represented by Rich (250). The latter author remarked that kaolinite in soils tends to be less crystalline than specimen material and may also display more evidence of isomorphous substitution.

Hydrous oxides

Correns (68) described the hydrous oxides as aqueous systems-- $\text{SiO}_2\text{-H}_2\text{O}$; $\text{Al}_2\text{O}_3\text{-H}_2\text{O}$; and $\text{Fe}_2\text{O}_3\text{-H}_2\text{O}$ --and observed that the Fe and Al systems were somewhat hydrophobic, tending to form gels which displayed little or no crystalline structure by X-ray diffraction.

The actual form of a given hydrous oxide in the soil is important since this determines the reactive potential of the oxide as shown by Van Schulerenborgh (306) and Sumner (288). Bohn (36) showed by solubility studies of $\text{Fe}_2\text{O}_3\text{-H}_2\text{O}$ systems in acid soils that in the pH range 4 to 8 $\text{Fe}(\text{OH})_2^+$ was the predominant form of the oxide. He argued that some $\text{Fe}(\text{OH})_3$ must be encountered as such in soils because of the rapid turnover of Fe due to factors such as microbial activity, redox reactions, complexation by organic colloids, and the time lag which is required for the precipitation of $\text{Fe}(\text{OH})_3$ from oxidized Fe^{2+} compounds relative to the rate of conversion of $\text{Fe}(\text{OH})_3$ to less soluble materials, such as Fe_2O_3 or Fe_3O_4 . Correns (68) emphasized the consequences of the fact that Fe can exist in two oxidation states. In aerobic conditions Fe is practically insoluble, and can be transported only as $\text{Fe}(\text{OH})_3$ sols. In anaerobic conditions FeCO_3 or Fe-humates of low redox potential can occur, and then on oxidation produce $\text{FeO}(\text{OH})$. Patrick (226) showed the existence of a linear relationship between pH and redox potential, and between the oxidation states of Fe and redox potential in anaerobic soil conditions. Such conditions do not always obtain, but it would seem that Fe supplied by the ultimate source--ferromagnesian minerals--accumulates in soils by the precipitation of Fe^{3+} forms transported in the reduced state as complexes with organic colloids (307). The precipitated forms can, with time, crystallize as geothite or lepidocrocite and may simultaneously incorporate co-precipitated $\text{Al}(\text{OH})_x$ into the structure. Hydrous oxides of Fe may be dehydroxylated to Fe_2O_3 or Fe_3O_4 or react with SiO_2 gels to form Fe-silicates (68). The $\text{Al}_2\text{O}_3\text{-H}_2\text{O}$ system has been widely studied. The initial sources

of Al are the K-felspars and plagioclases (307), and possibly kaolinite subjected to intense leaching or the action of humic acids (223, 149). The forms of hydrous oxides of Al in soils are determined by the degree of hydroxylation and, therefore, by the pH of the system. Van Schuylenborgh (307) considered that at pH 6 and above Al(OH)_4^- was likely to be the dominant form. Jackson (138), however, indicated that hydrous forms of Al began to polymerise at about pH 5, and that the isoelectric point of amorphous Al gels was at pH 8.3 in contrast to pH 4.8 for crystalline Al(OH)_3 . Somewhat at variance with this is the report that Al(OH)_3 precipitates only near neutrality (68). The most prevalent form of hydrous Al-oxide in soils is perhaps gibbsite, but Cate (52) concluded that its occurrence was determined by the leaching regime during the formation of the soil, with a period of dessication required for crystallization. In the presence of SiO_2 reactions may occur with Al hydrous oxides. Correns (68) stated that at ratios ($\text{Al}_2\text{O}_3:\text{SiO}_2$) of 1:2, kaolinite minerals tend to form, and usually the pH in such conditions is 4. With ratios of 1:3 or 1:4, 2:1 clays may develop. There seems little doubt that there is some association between amorphous hydrous oxides in soil, and that the nature of the association varies. Yuan (344) calculated that 0 to 16% of the total extractable Si and 17 to 64% of the Al in some Florida soils could be removed by citrate-bicarbonate-dithionite extraction. Weaver et al. (319) reported the extraction of greater amounts of Si, Al, Fe, and Mg by the same extractant from acid than from neutral or alkaline soils. The differential solubility of the amorphous materials was also reported by Tweneboah et al. (301), who extracted appreciable

quantities of Al but only small amounts of Fe and Si with 0.5M CaCl_2 at pH 1.5. Acquaye and Tinsley (2) mentioned the possibility of occlusion of SiO_2 by hydrous oxides of Al and Fe.

Organic Soil Colloids

Knowledge of the structure of the organic soil colloids--humus--is relatively less detailed than that of the inorganic colloids. This is due in part to the complexity of the material and in part to the indirect and destructive methods of study.

The organic fraction of the soil is usually measured by oxidative processes, but none of the methods available can be accepted as capable of providing accurate data. Weight loss detected on ashing oven-dry (105°C) soil at temperatures of 100-200°C, 375°C or 850°C was due principally to the oxidation of the organic fraction (18, 243). The loss of structural water may, however, contribute in varying degrees to the loss in weight of soil. Wet oxidation techniques (11) can provide precise measurements of the organic C content of the soil, but this has then to be converted to organic matter. Variations in the elemental composition of the organic fractions of different soils and different horizons within the soil are known to exist (159), and Broadbent (46) recommended that the standard correction factor of 1.724 proposed by Van Bemmelen be replaced by a factor of 1.9 for surface soils and 2.5 for subsoils in California. Ranney (243) concluded that 2.0 was a more appropriate correction factor for surface soils in Pennsylvania.

Fractionation of the organic material in soils has been based on alkaline extraction, usually with 0.5N NaOH. Martin and Reeve (181)

suggested that the alkali accomplished the prerequisite depolymerization of the large organic molecules and increased the dispersion of smaller polymers through the rupture of H-bonds. They regarded the conversion of Al^{3+} to AlO_4^- as the main step in the process since this prevented the flocculating action of Al. Levesque and Schnitzer (167) observed variations in the ash and C content of extracts with variations in the alkali concentration of the extractant. At alkali concentrations of 0.1N 70% of the soil C was extracted from the E_h of a podzol, but at 0.5N only 45% was extracted. Posner (236) concluded that there was an upper limit to the proportion of soil C which could be extracted, and that 0.5N NaOH extracts had the highest ash and C content as compared to pyrophosphate and bicarbonate extracts. About 10% of the soil Al was extracted by 0.2N NaOH (167), and Yuan and Fiskell (345) considered it likely that some of the Al would have come from the hydrous Al oxides in the soil.

Though determinations of the organic fraction are, at best, only approximations, the fractionation of the extractable organic material meaningfully reflects variations in composition. The components have been grouped according to variations in color, solubility, and molecular size. Felbeck (90) described them as:-

- (1) fulvic acids - lowest in molecular weight, lightest in color, and soluble in both acid and alkali.
- (2) humic acids - medium molecular weight and color, soluble in alkali and insoluble in acid.
- (3) humins - highest molecular weight, darkest in color, and insoluble in both acid and alkali.

Humins have received much less attention than the humic and fulvic acids. According to Kononova (159) they appear to be complexes of humic and fulvic acids not readily extracted by dilute alkali. This insolubility has been attributed to linkages with the mineral soil rather than to the occurrence of chemical alteration. Humins removed from soil have yielded humic acids with lower C, and higher H and O contents, and possibly of a simpler chemical nature than those readily alkali soluble humic acids (159).

Fulvic acids have been shown to be less aromatic (300), more acidic (336), and have less C (28, 159, 336) than humic acids. Schnitzer (267) postulated that 61% of the weight of the fulvic acid molecule was made up of functional groups with the ratios -COOH/-OH and -COOH/phenolic OH having values of approximately 1 and 3, respectively. He stated that fulvic acids were extremely resistant to biological degradation and usually contained appreciable amounts of carbohydrates. Tan and Clark (291) found a close association of fulvic acids and polysaccharides but virtually none with humic acids. They also noted that fulvic acid formed under grass was less lignoid and associated with more polysaccharides than that formed under pine.

Schnitzer and Desjardins (268) estimated that the molecular weight of organic material extracted from the A_o horizon of a podzol was 1,684 as compared to 669 for that from the Bh horizon. Each molecule from the A_o horizon was considered to have 6 carboxyls, 2 phenolic and 3 alcoholic hydroxyls while molecules from the Bh horizon had 3 carboxyls, 7 phenolic and 5 alcoholic hydroxyls. Wright and Schnitzer

(336) reported that the total acidity of 0.5N NaOH extracted material was 890 meq/100g and 1,180 meq/100g for the A₀ and Bh horizons, respectively. The former had 280 and the latter 210 meq/100g as phenolic hydroxyls. McKeague *et al.* (188) estimated 740 meq/100g as carboxyls and 360 meq/100g as phenolic hydroxyls in extracts from a spodic horizon. Wagner and Stevenson (316) used extracts from a brunizem soil and found that 30% of 390 meq/100g as carboxyls in the humic acids were close enough to form cyclic anhydrides, while > 60% of the 290 meq/100g as hydroxyls were phenolic.

Schnitzer and Skinner (271) established that alcoholic hydroxyls did not participate in reactions with metals and that the reactivity of the carboxyls varied. They indicated that two types of reactions which might occur with metals may include a major reaction with "salicylate structures" and a minor reaction with the less acidic carboxyls. Martin and Reeve (183) described the flocculating effects of Al on organic matter, and suggested that some reactions might involve electrostatic bonding while others utilized coulombic forces (182). The reactions in which humic acids engage are influenced by the pH and the cation. More Fe and Cu and less Al reacted with humic material at pH 5.0 than at pH 3.5 (271). Posner (235) observed that while Ca^{2+} flocculated humic acids at ionic strengths $\geq 0.0023\text{M}$, K^+ formed no specific complexes. Ling Ong and Bisque (175) reported that the flocculating effects of cations increased as the radius of the hydrated ion decreased. They established that ionic concentrations required for flocculation varied with valence in the order: monovalent : divalent : trivalent = 1.0 : 0.014 : 0.0014. The effect

of anions associated with K^+ decreased in the order $SO_4^{2-} > NO_3^- > Cl^-$.

The variation in acid strength of the carboxyls in humic acid (269) was found by Posner (235) to follow a Gaussian distribution about a mean pK value of 5.5 ± 1.7 . He concluded that this phenomenon was responsible for the atypical electrolytic behavior of humic acids. Gilmour and Coleman (107) regarded the smaller charge density and the micromolecular structure of humic acids in the presence of monovalent cations as the reason for the atypical behavior. Martin and Reeve (182) reported that the apparent pK values of humic acids varied with the C/Al ratio of the material. At a ratio of 4.9 the pK value was 6.2, but dropped to 4.1 at a ratio of 152. This implies that the more acidic functional groups are the first to be neutralized, but Posner (236) was of the opinion that lower pK values were obtained when humic acids were bound to Al, Fe, or Ca.

Various functional groups in the organic fraction have been estimated to contribute different amounts to the total charge. Broadbent and Bradford (47), and Schnitzer and Skinner (269) attributed 55% of the charge to carboxyls, while 35% have been attributed to phenolic hydroxyls, and 10% to imide-N (106). The contribution made to soil reactions by the different categories will vary with conditions. Lewis and Broadbent (169) suggested that some carboxyl groups may have reacted with $Cu(OH)^{2+}$ while phenolic groups complexed Cu^{2+} . Schnitzer and Skinner (271) pointed out the simultaneous action of some carboxyls and phenolic hydroxyls. This and the distribution of pK values emphasize the importance of soil reaction in this context.

According to Broadbent (46) the composition of the organic fraction

varies with the environment and the material from which the humus forms. Absence of periods of dessication and the predominance of hydrolytic processes inhibit condensation to humic acids and favor the formation of fulvic acids (159). Coulson *et al.* (69) reported that acidity inhibited the oxidation and polymerization of polyphenolic products of decomposition, but Wright and Schnitzer (336) concluded that humic acids could be converted to fulvic acids by an increase in the number of O-containing functional groups, e.g., -COOH. Alexandrova (9) found that the process of humification involved an increase in carboxyl content and a simultaneous decrease in phenolic hydroxyls. These changes proceeded simultaneously but at different rates and to different degrees, depending on the type of material involved. The elemental composition of the final products of humification was determined primarily by the type of material and its chemical composition (10).

Differences in the relative amounts of humic and fulvic acids have been shown to exist in the soil and to be related to the horizons (292, 336, 343). Several workers have also attempted to relate the composition of the organic colloids to soil type. Tan and Van Schuylenborgh (292), and Tan (290) found that the latosols of Indonesia had much higher proportions of fulvic acids than of humic acids. Niu Ching Wén (214) reported similar findings for lateritic and red earth soils of tropical and subtropical China, as did Tokudome and Kanno (300) for red-yellow soils of Japan. Kononova (159) described similar properties in acid, leached soils on the Black Sea coast. Ponomareva

(233) suggested that brown, red or yellow soils tended to have higher proportions of fulvic acids than did grey or black soils. Zonn (348) extended this idea and classified the forest soils in the U.S.S.R. in terms of their proportions of fulvic and humic acids.

Inorganic Interaction

Sumner (288) demonstrated that ferric oxides and kaolinite form complexes which differ in charge from the original kaolinite component. The charge on the mineral is normally constant from pH 2.4 to 5, but addition of ferric oxide caused a decrease in the negative charge at pH < 6, and an increase at higher pH levels. Follett (92) reported that the Fe-oxide was sorbed on the tetrahedral surfaces only, by an apparently crystallographically specific reaction which was unaffected by excesses of NH_4^+ , Ca^{2+} or Al^{3+} . Greenland and Oades (110) found that the form of the oxide determined the mechanism and degree of sorption that took place. The purity of the oxide was also important since sorption of SiO_2 or organic matter could produce a net negative charge on the Fe-oxide and inhibit reaction with clay crystals. Most of the free Fe-oxides occurred in the fine clay soil fraction (282).

Jackson (138) indicated that the polymers of hydrous Al oxides could be adsorbed on clays through oxygen atoms in functional groups. Precipitation of hydrolyzed exchangeable Al on exchange sites was considered likely (64), as was the deposition of hydroxy-Al units on the surfaces of clays or other crystals (240). These mechanisms and the possibility of hydrous Al oxides occurring as impurities in hydrous Fe oxides represent the major means of Al involvement in interaction of

inorganic colloids in soils.

Organic - Inorganic Interaction

Interaction between kaolinite and organic colloids was studied by Evans and Russell (88). They reported that kaolinite sorbed more fulvic than humic acids and that the sorption of fulvic acids was enhanced by ions in the order $\text{H}^+ > \text{Ca}^{2+} > \text{K}^+$, while humic acid sorption was enhanced by ions in the order $\text{Ca}^{2+} > \text{H}^+ > \text{K}^+$. They suggested, as did Martin and Reeve (183), that the presence of exchangeable Al facilitated the adsorption of organic colloids on the clay. The latter authors noted in Al-bentonite systems that the sorption of organic material was complete at pH 2 to 3, but decreased to about 50% at pH 6.

The likely natures of bonds between organic colloids and clays were described on the basis of data from humic acid-Ascanit models by Alexandrova (8). She characterized the interaction as aggregation by coalescence with the involvement of some intermolecular and H-bonds. Coalescence was enhanced by Ca^{2+} and reduced by adsorbed water. The involvement of intermolecular and H-bonds was also suggested by Fripiat (101). Mortensen and Himes (204) stated that hydroxyl groups, mainly on the basal surface, were possibly involved through the formation of polar and non-ionic compounds. Fripiat (101) indicated that bonds likely to be formed would have degrees of stability varying in the order: $\text{Si-O-H} > \text{Si-O-N} > \text{Si-O-C}$, and that monomolecular films of water would form bridges between the clay and the organic colloid in the complexes. The possibility of bonding between carbohydrates and exposed lattice

Al, or of coordination with adsorbed or lattice Al, was mentioned by Mortensen and Himes (204). Purely ionic bonds between organic colloids and clays seem to have been ruled out.

With hydrous oxides and organic colloids, interaction is regarded as involving the displacement of H^+ from carboxylic groups by $R(OH)^{2+}$, where R represents either Al or Fe (10, 270). Greenland (109) classified the mechanisms of interaction as coulombic attraction, coulombic forces, and ligand exchange reactions. Infra-red spectra indicated that electrovalent bonds were formed (270), but Alexandrova *et al.* (10) regarded the bonds as being coordinate in nature. Schnitzer and Skinner (270) showed that the molar ratio--metal/organic colloid--varied with pH. At pH 5 the molar ratio was about 3, but increased with pH as the organic colloid was replaced by OH ions. With a molar ratio of 3, $R(OH)^{2+}$ was the postulated ionic form of the hydrous oxide. Examination of extracts from a podzol B horizon gave molar ratios of 2.8 (336), and hydrous oxide of form $R(OH)_2^+$ (188). Organic colloids of the podzol B horizon were found to contain 85% fulvic acids and to be immobilized only when all the functional groups were engaged (336). Ponomareva (233) stated that the organic matter-hydrous oxide complexes had pH values in the range 4 to 6, essentially agreeing with Waksman's (317) concept of β -humus which gave the soil its buffering properties, was precipitated at pH 4.8, and consisted largely of ash.

Organic matter has been shown to be flocculated by Al (183), and by Fe (184) but Tan (290) found greater saturation of organic colloids by Fe in the surface horizons, and by Al in the lower horizons of some Indonesian latosols. This confirmed the earlier conclusion (292) that

Fe was preferentially complexed by humic acids and Al by fulvic acids. Titova (299) established that humic-Fe complexes were immobile in an electric field at pH 8.5 while fulvic-Fe complexes in similar conditions yielded a precipitate of $\text{Fe}(\text{OH})_3$ and a mobile Fe-organic complex. D'Yakonova (83) indicated that complexation of Fe by organic colloids increased from about pH 2 and decreased above pH 4, but above pH 4.0 the proportion of mobile fulvic-Fe complex decreased and that of immobile Fe-humic complex increased.

Alexandrova *et al.* (10) described the OM-metal complexes as "complex heteropolar salts" and indicated that complexed Fe lost its cationic properties completely and complexed-Al only partially. Part of the Al remained exchangeable. They showed that the OM-metal complexes displayed a "pH effect" during potentiometric titration. The pH range of buffering differed with the metal and the organic colloid. Humic-Fe complexes were buffered in the pH range 3 to 6, and humic-Al complexes in the pH range 6 to 10. Dialysis of the complexes raised the range of buffering to pH 6 to 10 for both complexes. Fulvic-Fe complexes were buffered in the range pH 2 to 6 and fulvic-Al complexes in the range pH 2 to 5. Dialysis of these complexes shifted the range of buffering to pH 6 to 10. Yuan (341) reported that on acidification of 0.5M NaOH extracts from the organic pans of three Florida soils, precipitation began at pH 7, and increased with increasing acidity to a maximum at pH 4.0 to 5.5. He considered this precipitation to be due to Al.

The effect of complexation of the hydrous oxides by the organic colloids was also shown by Alexandrova *et al.* (10) to result in a marked

depression of the negative charge on the organic colloid. This effect was much stronger where Al was complexed than was the case with Fe. The stability of these complexes was shown to vary not only with pH but also with the redox potential of the system (8), and with the cation (48). Complex formation was found to be a rapid process, limited by the rate of diffusion of cations into the solid phase (48). Khanna and Stevenson (151) concluded that the entrained metals masked the chelation sites of the organic material.

Nutrient Retention

The net results of the interaction of soil colloids are reflected in the physical properties of soils through the nature and persistence of their cementing agents, and, therefore, through their structural conditions. The effects are, however, more readily seen in chemical phenomena, principally pH, the relative importance of the various forms of Al, and the capacity of the soil mass to retain nutrients. Retention of nutrients is effected through surface phenomena by which fixed charges on the surface are countered by ions of opposite charge in the adjacent layers of solution, at the interface between the solid particle and the liquid. This is the electrokinetic effect--the double layer (43, 223). Retention is also effected by means of Donnan effects involving macromolecules which tend to remove electrolytes from the solution in order to maintain electroneutrality in the medium. Charges are fixed within the macromolecule as well as at the surface. The internal charges are neutralized by the diffusion of counter-ions into the gel, and the nature of these charges determines whether the external

solution develops an alkaline or an acid reaction (43).

The relative amounts of the different soil colloids determine the contribution to nutrient retention mechanisms attributable to electrokinetic or Donnan effects. The clay minerals invoke electrokinetic effects while the organic colloids (106) and the hydrous oxides of Al and Fe are gelatinous and likely to invoke Donnan effects (43, 68).

Thomas (296) described some red-yellow soils of North Carolina as being both salt sorbers and cation exchangers. He reported the imbibition of electrolyte by these soils with the consequent reduction in salt movement and salt concentration in the soil solution, as well as the influence of anions on the retention of sorbed cations. His data suggested that a prominent role is played by organic matter and the products of its interaction with hydrous oxides. Oliveira *et al.* (222) concluded that the retention of K by some Brazilian Ultisols was possibly associated with amorphous alumino-silicates. Van Reeuwijk and De Villiers (304) showed that such an association was possible, and apparently involved normal exchange sites rather than precipitation or other specific chemical reactions. They reported that the retention of K by this mechanism was pH-dependent and decreased in extent with increase in Al content of the Al-Si gels. Muljadi *et al.* (208) reported the penetration of K-phosphate into less crystalline portions of kaolinite. Electrokinetic effects are generally considered to provide the most important mechanisms of retention of both anions and cations. Such mechanisms do not normally result in alteration of the chemical form of the charged surface, and ions are reversibly adsorbed.

Cation Sorption

The capacity of a soil for retaining cations in exchangeable form is usually described as its cation exchange capacity--CEC. This capacity was shown to be the sum of sites of permanent negative charge (265), and of those sites which develop a negative charge at a given pH. The cations which usually counter the negative charges in soils include $(Al)^+$, H^+ , Ca^{2+} , Mg^{2+} , and K^+ . Of these, the various forms of Al indicated above as $(Al)^+$ and H^+ are considered sources of acidity and, therefore, undesirable. The remaining cations vary in quantity depending on soil type and soil reactions, but collectively constitute the degree of base saturation of the soil. The generally undesirable consequences of acidity underline the importance of the degree of base saturation and the controversy which surrounds the pH level most appropriate for CEC measurements.

Bradfield and Allison (41) found that soils in equilibrium with the atmosphere and having a pH value of about 8.2 were completely base saturated. Mehlich (192) and Clark and Hill (58) observed that base saturation-pH relationships varied with soil type, but the buffered $BaCl_2$ - TEA method of CEC determination at pH 8.2 was shown to give maximum values and to include a component due to the anion exchange properties in soils rich in hydrous oxides. Coleman *et al.* (63) measured the "effective" CEC at the pH of the soil with a neutral unbuffered salt and found that it included some pH-dependent sites. This was confirmed by Bhumbra and McLean (29) who compared the N KCl, NH_4OAc (pH 7.0) and $BaCl_2$ -TEA (pH 8.2) methods of CEC determination. The N KCl-CEC accounted for 30 to 70% of the $BaCl_2$ -TEA CEC at pH 8.2

in red-yellow soils, and the actual proportion was believed to be determined by the extent to which the soil particles were coated with Fe-oxides (66, 190) or Al oxides (65). The NH_4OAc -CEC method at pH 7.0 gave values intermediate between the N KCl and $\text{BaCl}_2\text{-TEA}$ (pH 8.2) methods (29) probably because it included more pH-dependent sites than the N KCl method, but fewer than the $\text{BaCl}_2\text{-TEA}$ (pH 8.2) method.

In addition to the pH of measurement, the saturating ion also affects the measured CEC values. Variations in values with the valence of the saturating ion were reported by deEndredy and Quagraine (76). With monovalent ions, CEC was independent of pH in the range 7 to 8, but varied with pH in this range when divalent ions were used. They concluded that the ratio monovalent CEC:divalent CEC was dependent on the clay type, and to a lesser extent on the organic colloids. However, Bhumba and McLean (29) reported that the difference between values obtained using NH_4^+ and Ba^{2+} as saturating ions was highly correlated with the amount of organic matter in the soil. This correlation can probably be explained by the idea (76) that monovalent saturating ions may have caused the dissolution of some of the potential exchange sites in the soil since the alkali salts of organic colloids are soluble, whereas similar alkaline-earth salts are relatively insoluble. Alternatively, at the higher pH levels incompletely hydrolyzed hydroxides of divalent alkaline earth metals may be adsorbed (53), possibly by phenolic hydroxyls of the organic colloids (169, 213), thereby over estimating the CEC. The likelihood of this is strengthened

by Posner's (235) findings that humic acids had a higher CEC at pH 3 to 7 with divalent than with monovalent cations.

Reeve and Sumner (248) introduced the concept of "net" CEC based on an Al-equilibrium rather than on pH, per se. The criterion here is exchangeable Al, but in effect the concept seems to be closely parallel to "effective" CEC. Their allusion to free hydrous Al-oxides, exchangeable Al, and Al-organic matter complexes in the context of CEC is apparently justified by the findings by Frink (102) that the change in CEC on removal of sequioxides from the soil by citrate extraction was highly correlated with the Al removed, but not with Fe removed. Pratt (237) stated that neutral salts did not replace pH-dependent acidity, and that CEC was only increased after the acidity was released by an increase in pH. Bhumbla and McLean (29) noted a twofold increase in N KCl -CEC after liming, and the change was attributed to the release of Al from previously occupied exchange sites. The efficiency of K as the saturating cation is perhaps related to the large affinity for K displayed by acid clays either with a low degree of K saturation or largely Al-saturated (218).

Cation Retention Patterns

The total amount of adsorbed cations is determined by the CEC of the soil, but the proportions of the individual cations vary with the bonding preferences obtaining in the soil. The strength with which a given cation is held will vary with the nature of the colloid, the degree of saturation of the colloid, and the nature of the complementary ions (84, 325). The type of colloid influences the strength of bonding through the location, and density of charge (325). Wiklander (325)

showed that the acid strength of the site varied with the location of the charge and that at pH 6.1 hydrolysis occurred more readily than at pH 4.9 to 6.1, so that cations held by sites which are functional only at pH values higher than 6.1 are likely to be more easily lost (324).

In the case of crystalline clays all negative charges act at the surface (223, 250), through coulombic attraction, and the bonding strength for a given ion at a given site varies with valence and hydration radius of the ion. The order of strength of bonding can be expected to be $\text{Al}^{3+} > \text{H}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$ (325). Wiklander and Ghosh (326) showed that kaolinite bonded Ca^{2+} relatively weakly. Eck et al. (84) concluded that at saturations greater than 45 to 60%, kaolinite readily released Ca^{2+} to plants.

With organic colloids, the functional groups are not necessarily superficial and the solubility or stability patterns of organic matter-metal complexes may become more important than the ionic double layer. Alexandrova et al. (10) indicated that Ca^{2+} , Mg^{2+} , and K^+ can be bound by organic colloids in soluble or insoluble heteropolar salts, and Kononova (159) pointed out that the fulvates and humates of alkali metals are soluble at all pH levels, while alkaline-earth humates are less soluble, Ca-humate more so than Mg-humate. Schnitzer and Skinner (272) reported that fulvic acids complexed divalent ions with the order of stability $\text{Cu}^{2+} > \text{Fe}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$ regardless of pH, but that the molar ratio, metal/fulvate, increased with pH. Broadbent and Ott (48) obtained a similar order of stability, $\text{Cu}^{2+} > \text{Ba}^{2+} > \text{Ca}^{2+} \geq \text{Mg}^{2+}$, with organic matter extracts. It is noteworthy that only the carboxyl

groups of the organic colloids are dissociated at pH less than 7.0 (159).

Taking the soil as a whole, Spencer (284) established that in soils in which more than 75% of the CEC was contributed by the organic fraction, cation adsorption patterns were different from those in soils with larger proportions of inorganic CEC. Yuan *et al.* (346) related the size of the contribution to the soil CEC made by the organic fraction to soil type. They obtained values of 96% for Spodosols as compared to 67% for Mollisols in Florida. The pH-dependent nature of the contribution to the soil CEC by organic matter was demonstrated by Helling *et al.* (120). In soils of high organic CEC, Ca^{2+} and H^+ compete strongly for exchange sites excluding K^+ completely, and Mg^{2+} to a large degree (289). McGeorge (187) demonstrated that the affinity of organic matter for K^+ was very low compared to that for Ca and Mg ions. Mehlich (193) considered that K^+ was barely held by exchange sites in organic matter and Gammon (104) concluded that most of the K in cultivated sandy soils in Florida was in the form of soluble salts rather than adsorbed on the exchange complex. Organic matter held Ca more strongly than kaolinite (200), but substantial quantities of water soluble organic matter-Ca complexes have been found in soils (213). Hydrous oxides also modify cation retention patterns. Mehlich (195) noted that hydrous Al-oxides increased the amount of Ca^{2+} in solution and suggested that the oxide affected the nature of the bond between Ca^{2+} and the exchange site. There seemed, however, to be no effect on the ease of release of Ca^{2+} , by the oxide. Hunsaker and Pratt (134) observed that there was a marked preference for Ca^{2+} over Mg^{2+} adsorption

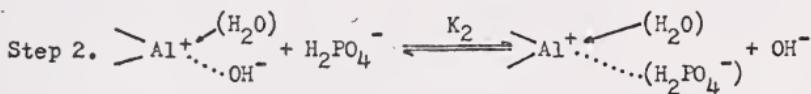
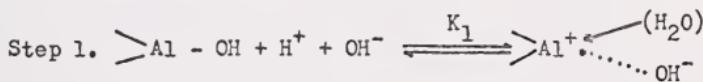
in red latosols, but no indications were given as to the relative effects of the organic matter and the hydrous oxides present. Hydrous oxides were considered to be involved in the equilibrium, exch-K \rightleftharpoons non-exch-K, thought to exist in Brazilian Ultisols (222). The low supply of exchangeable K in highly weathered soils may possibly be related to the existence of such an equilibrium or to the capacity of these soils for electrolyte sorption (296), but Graham and Fox (108) found high correlation between labile K and rainfall in similar soils. This conceivably derives from the soluble nature of salts of K and the organic colloids, and to the greater freedom of movement of K in Al saturated sandy soils (297). In sandy soils the movement of K was increased by increase in soil pH (313, 324), with K moving primarily as KNO_3 and K_2SO_4 (313).

Anion Sorption

The sorption of anions by soils has been described by Wiklander (325) as comprising the processes of negative and positive adsorption. He indicated that negative adsorption of anions is due to mutual repulsion of similarly charged particles and that it is influenced by the nature of the charged surface, the hydration of the ions, the salt concentration, and the pH level of the soil. Negative adsorption results in a deficit of anions in the immediate vicinity of the charged surface, and thereby facilitates the loss of anions by leaching (325). Positive adsorption is due to electrostatic attraction and chemical bonding, with bonding strengths increasing in the order $\text{NO}_3^- = \text{Cl}^- < \text{SO}_4^{2-} < \text{PO}_4^{3-}$ (27). In addition to the role of

the ion itself, positive anion adsorption is influenced by the nature of the charged surface and the pH of the medium (325).

Berg and Thomas (27) found that all sites which held anions were pH-dependent in effect, and considered the process of adsorption to be the result of displacement of hydroxyl groups. Samson (264) demonstrated that the process of positive anion adsorption involved the exchange of hydroxyl groups of the octahedral layer of clays by the anion, and that the process was limited by the availability of hydroxyl groups. His computations showed kaolinite to have a higher concentration of hydroxyl groups than montmorillonite. Schofield and Samson (266) attributed the increase in anion adsorption at low pH levels to proton sorption, and, on the basis of this, Muljadi *et al.* (206, 207) proposed the reaction:



in which \longrightarrow indicates coordinate, and $\cdots \cdots$, electrovalent linkages. Hingston *et al.* (123) constructed adsorption 'envelopes' for different anions on goethite and deduced that the mechanism of adsorption varied with the anion. They found that non-protonated ions did not influence the charge on the surface, and were sorbed in the diffuse double layer so that the proportion of the anion in solution was the same as that sorbed. When the anion was partially protonated, it had the capacity to either accept or donate a proton to the surface, and could, therefore, modify the charge on the surface. When the partially protonated anion increased the negative charge on the surface, it was

bound to the surface to a greater extent than would be expected from its proportion in the solution. The anion formed a coordinate linkage with the metal rather than with the hydroxyl, and the extent of its sorption was maximal at the pK value of the corresponding acid species (123). Jones and Handreck (144) also implicated protons in the sorption of $\text{Si}(\text{OH})_4^-$, but considered this different to the sorption of H_2PO_4^- which was bonded through oxygen atoms.

The effects of anion sorption in soils have been reported by various workers. Schuffelen and Middleburg (273) characterized the release of OH^- by anion sorption as "exchange alkalinity." Mehlich (194) observed an increase in negative charge and formulated the concept of the CEC:AEC ratio. He regarded CEC measured after phosphating the soil as the maximum CEC (196), and later concluded that anions were differently bound. His conclusion was that Cl^- remained in the ionization sphere countering positive charges while SO_4^{2-} and H_2PO_4^- entered the coordination sphere (197), but H_2PO_4^- did not add very much to the anion exchange acidity of the soil (198). Bar-Yosef et al. (24) theorized that either the anion did not replace OH^- or the displaced OH^- remained bound to the surface.

Kinjo and Pratt (152) found that NO_3^- sorption on a Brazilian Oxisol decreased to zero with increase in pH to 5.5, but that the neutralization of replaced NO_3^- by H^+ was not stoichiometric. They established that amorphous materials were responsible for NO_3^- sorption, and considered the non-stoichiometric relationship to be due either to an inherent difference in anion sorption by soils dominated by Al and Si rather than by hydrous oxides or to the CEC:AEC ratio of the

soil. They found also that though SO_4^{2-} replaced NO_3^- in a stoichiometric manner, there was a 0.5 to 1.0 unit increase in pH. A 1:1 replacement of NO_3^- by H_2PO_4^- was obtained initially, but this changed to values of 1:3 or 1:4 indicating that P reacted with two or more sites not available to NO_3^- (153). They noted that P enhanced the negative adsorption of NO_3^- at low pH levels, and concluded that some charged sites had different affinities for different anions. Muljadi *et al.* (209) reported differences in affinity for P by different sites, and concluded that the process of adsorption resulted in an entropy change.

Phosphate Retention in Soils

Phosphate retention is frequently used interchangeably with phosphate fixation, but it seems preferable to reserve the latter term for those processes which reduce the availability to plants of retained phosphates.

Bradfield *et al.* (42) described P retention as being due to a wide range of reactions which involved distinct but overlapping mechanisms. Kardos (148) summarized the mechanisms as adsorption, double decomposition, and isomorphous replacement. Low and Black (176, 177) reported that P replaced Si in kaolinite in acetate systems at 60°C buffered at pH 4.5, and at 45°C buffered at pH levels in the range 4.5 to 5.1 by dissolution and precipitation according to solubility product principles. Reifenberg and Buckwold (249) obtained replacement of Si by P at room temperature in the pH range 6.8 to 8.5. They noted that the degree of replacement was higher in finer than in coarser

textured soils, and that at pH 7.5, the effect of pH was minimal. The replacement of Si increased with increase in P concentration, and with time. Kafkafi *et al.* (146) found P retained by kaolinite to be isotopically exchangeable initially, but to become irreversibly bound on washing. With larger amounts of P, some Si was replaced and more of the added P was irreversibly held. Hsu (129) interpreted his data to mean that Fe-P formed on decomposition of Fe-silicates, but considered the process a surface reaction at pH 6.4 to 7.0.

Kittrick and Jackson (156) examined the reaction of P and hydrous oxides and concluded that P retention was generally due to chemical precipitation. Hsu and Rennie (131) reported that P retention comprised two reactions which differed largely in rate; the first and main reaction was rapid, and was followed by a slow double decomposition process. Coleman (61) also detected two reactions, but found the slow reaction to occur at pH < 5, and the rapid reaction at pH > 5. He did not observe any replacement of Si from the clay minerals, and attributed all P retention to the hydrated oxides coating the clay minerals. Hsu (130) reasoned that P retention by hydrous Al oxides did not involve precipitation, but rather surface adsorption, since there was no obvious destruction of the initial surface.

Eriksson (86) concluded that P retention was probably due to a physico-chemical process by which OH ions, possibly from sesquioxides, were exchanged for P ions, or to a purely physical process of polar adsorption to soil particles. Bache (17) distinguished three stages in P sorption: a high energy chemisorption process, precipitation of

a separate phosphate phase, and a low energy sorption of P on the precipitate. Hsu (130) argued that physical adsorption played little, if any, part at all in P retention, but Bache (17) indicated that physical adsorption could occur and that the process was reversible, involving a small decrease in energy. Chemisorption was considered (17) as being partly or completely irreversible and involving a large decrease in energy, while precipitation of P occurred only in the presence of large amounts of P to give products such as (Al, Fe)
 $(H_2PO_4)_n(OH)_{3-n}$ where n = 1 at pH < 3.5 for Al and < 1.5 for Fe, but n < 1 at higher pH levels. Bache (17) also indicated that some P could diffuse into the solid hydrous oxide phase. Muljadi *et al.* (206, 207, 208) described three regions in P adsorption isotherms and suggested that region I reflected the adsorption of P by the replacement of the first hydroxyl of $Al(OH)_2$ groups, region II corresponded to the replacement of the second hydroxyl, and region III was due to the penetration of P into the solid phase. Regions I and II were governed by the Langmuir isotherms while region III was a linear isotherm.

Adsorption of P in all three regions was apparently reversible with respect to pH in the range 5 to 9 for kaolinite, but only partly so with respect to concentration in regions II and III and not at all in region I. With hydrous oxides, adsorbed P was much less reversible than with kaolinite in regions II and III. The number of sites of P sorption in regions I and II reached a maximum at pH 5, while those in region III were maximal at about pH 7. The shape of region III isotherms was interpreted to mean that either the number of sites remained constant

despite increases in the amount of sorbed P, or the number of sites was large compared to the amount of P sorbed. The pH of the medium did not appear to influence the proportion of sites in regions I and II.

Though the mechanism of P retention is apparently the same for different surfaces, the amount of P retained varies with the size of particles and their degree of crystallinity. Colwell (67) attributed P retention to the extent of 7.34% and 0.05% (w/w) by amorphous hydrous Al oxides, and gibbsite, respectively, to differences in particle size. Muljadi *et al.* (207) found that at pH 3.0 kaolinite sorbed 2.95mM P/100g while gibbsite sorbed 45mM P/100g. Fox *et al.* (93) reported that the intensity of P retention decreased in the order: amorphous hydrated oxides > cryptocrystalline goethite > gibbsite > kaolinite > 2:1 clays; with pH 5 to 6 permitting optimum P solubility. Ross and Turner (258) found the rate of crystallization of $\text{Al}(\text{OH})_3$ to be affected by the presence of anions. The effects varied with the size and structural complexity of the anion. Juo and Ellis (145) indicated that colloidal precipitates of Al-P and Fe-P formed rapidly. The Al-P colloids crystallized more slowly and had greater surface area than Fe-P.

Sorption of P by organic matter-Fe complexes was reported by Weir and Soper (320), and by Levesque and Schnitzer (168). The latter authors indicated that P was bonded to the metal--Al or Fe--in fulvate complexes and could replace fulvate groups. The amount of P thus retained varied with the C content of the complex, lower C contents permitting higher P sorption.

The degree of overlapping of the different mechanisms is, no doubt, dependent on the composition and reaction of the soil. Soil reaction governs the ionic form of the hydrous oxides present and the availability of divalent cations. Its importance is reflected in the postulate by Bradfield *et al.* (42), that at pH 2 to 5, P was retained in soils as precipitated Al and Fe phosphates; at pH 5 to 7, P was adsorbed on clay surfaces; and at pH 6 to 10, P reacted with divalent cations. Wild's (327, 328) conclusion differed somewhat from this, but reiterated the influence of pH on the mechanisms of P retention. He concluded that at pH levels < 3 to 3.5 P was retained by Fe, and that Al-P formed at pH 6 to 7. Chang and Jackson (55) observed that on addition of phosphate to a podzol at pH 5 Al-P and Fe-P increased. They also observed the formation of Ca-P at higher pH levels as suggested by Bromfield (49). Lucas (178) reported increases in Al-P and Ca-P with addition of P to an amorphous soil. Increases were more marked for Al-P than for Ca-P, while Fe-P decreased. Yuan *et al.* (347) noted initially that the Al-P and water soluble P increased while P additions left Ca-P unchanged, but decreased the percentage of P as Fe-P and Ca-P. Shelton and Coleman (275) found that added P was retained in red clay soils as Al-P and Fe-P for more than 6 months with a greater fraction initially as Al-P. Chang and Chu (56) considered the moisture content of the soil to influence P retention. On relatively dry soil, P was retained mainly as compounds, with relative amounts decreasing in the order Al-P > Fe-P > Ca-P, regardless of pH. Prolonged contact caused Ca-P and Al-P to change to Fe-P, and the rate of change increased with

increased moisture. Eriksson (86) distinguished between octo-P and ortho-P of Ca, pointing out that the latter, though more soluble, formed only in the presence of relatively large excess of Ca. The possibility of formation of Ca-Al-P compounds was indicated by Taylor *et al.* (295) and by Huffman *et al.* (133).

The role of hydrous oxides in P retention by soils is influenced by several additional factors, such as, the form of the oxide, its relative quantity and solubility, and the presence of competing ions. Hsu and Rennie (132) observed that exchangeable Al, held by a resin, was precipitated by P, and Coleman *et al.* (62) obtained high positive correlation between exchangeable Al and P sorbed by soils. Tandon (293) estimated that 5 or 6 Al atoms were involved in the retention of one P atom, and suggested that the Al was in polymeric form. He obtained better correlation between NH_4F extractable P than total P, and NH_4F extractable Al, indicating that all P was not retained by Al. Williams (330) reported positive correlations between P retention and hydrous Al-oxide content of soils, but noted that the role of the oxide was modified by pH and organic matter content. The $\text{Al}_2\text{O}_3:\text{Fe}_2\text{O}_3$ ratio also affected the role of hydrous Al-oxides in P retention (295, 330). Having observed some correlation between P retention and organic matter content, Williams (330) suggested that Fe-organic matter complexes may have been involved. LeMare (166) also obtained correlations with pH, organic matter content, and P potential. Halstead (118) found that organic P was associated with Fe-P, but that Al-P was the major form of P in the silt and fine clay fraction, except in podzols where Fe-P predominated. He found by the

fractionation procedure of Chang and Jackson (54) that salloid-P, Al-P, Fe-P, and Ca-P accounted for 62 to 92% of the inorganic P with Ca-P being the major form of P in all soils except podzols.

Ramulu *et al.* (244) found a closer relationship between oxalate extractable Fe and P "fixation" than with dithionite extractable Fe. Boiling 0.1N NaOH extractable Al was highly correlated, 0.1N HCl extractable Al very poorly correlated, and N KCl (pH 2.0) very well correlated with P "fixation." However, N KCl extracted < 1.0% of the soil Al (244). Yuan (342) found 0.1N HCl extractable Al to be highly correlated with the P sorption capacity of some Florida soils, and Lucas (178) obtained good correlation with P sorption and both N NH₄OAc (pH 4.8) and 0.1N HCl extractable Al. Correlation with the latter was somewhat better. Puri and Swarnakar (238) reported similar trends in extraction of Al, Fe, and P by N KCl at different pH levels. Minimum values were obtained in each case at pH 6 to 7. Halstead (118) observed that oxalate soluble Al and Fe were related to P retention, but closer relationships were more evident with Al in neutral soils and with Fe in acid soils.

The influence of competing ions on P sorption was shown to vary with the pH, the anion, and the soil type by Deb and Datta (73, 74). The pH of maximum effect of any anion was the pH of maximum stability of the complex it formed with the adsorbing surface (73). At pH 6 SiO₂ was most effective in replacing P, but its effect was greater in alluvial than in red soils. Citrate was most effective at pH 7 (74). Acquaye and Tinsley (2) suggested that SiO₂ might influence the P status of a soil, but that this influence was reduced by humus at pH 6 to 9,

since humus enhanced the solubility of SiO_2 in that pH range. Beckwith and Reeve (25) reported the increased sorption of Si with increase in pH, but Jones and Handreck (144) doubted the efficiency of Si(OH)_4 in reducing the sorption of P. Hingston *et al.* (123) demonstrated that the competition between P and other anions was more akin to desorption than to exchange. The desorptive capacity of an anion was dependent on the pK value of the corresponding acid. Silicic acid had a pK of 9.2 while H_2PO_4^- had a pK of 6.5 (123). Fulvic acid was shown by Leaver and Russell (163) to compete effectively with P at pH 5.5, but Levesque and Schnitzer found that the effectiveness of fulvates decreased as pH increased (168). This agreed with the concept of maximum adsorption near to the pK value (123). Hesse (122) concluded from studies in mangrove swamps that P was retained by organic matter, but the necessary role of a metal was stressed by Wild (328) and Levesque and Schnitzer (168). Fox and Kamprath (96) failed to obtain any appreciable P retention by organic matter in the absence of complexed cations.

Nutrient Availability and Plant Uptake

The availability of nutrients to plants is governed to a large degree by the amount and chemical form of nutrients retained by the soil. This in turn influences the amounts taken up by the plant. The stage of growth (302) and the moisture regime which obtains during the development of the plant (339) also modify nutrient uptake. Generally, the plant exerts some influence on the chemical form and concentration of nutrients in the immediate vicinity of the roots (20, 253, 259,

278), and may thus effectively increase the availability and uptake of nutrients. Rovira and McDougall (259) stated that a layer of mucilaginous material on the epidermis extended the ion-exchange zone of the root by virtue of its COOH groups, and that root excretions could help to increase the solubility of several nutrients in the soil. Root excretions are largely organic acids (259, 278) which Stevenson (286) indicated in his discussion, were capable of lowering the pH and forming complexes with Ca, Mg, Al, and Fe. Their effects may be important only in localized zones near decomposing material or actively growing roots (259), but do not significantly alter conditions in the soil as a whole. Riley and Barber (253) reported salt concentrations in the rhizosphere of soybean plants 5 to 15 times greater than those in the non-rhizosphere soil and suggested that the concentration of cations in the roots was regulated by the physiology of the plant rather than by the supply to the roots. Barber and Ozanne (20) found an increase of 1.0 pH unit and a 7-fold increase in Ca^{2+} in the rhizosphere of soybeans and concluded that HCO_3^- had been excreted by the roots. Rains *et al.* (241) mentioned the possibility of competition between HCO_3^- , OH^- , and other anions for plant uptake at higher pH levels.

The high number of variables in P availability and the frequency with which this element has been found to limit plant growth have resulted in the expenditure of much time and effort in the study of P availability. Jackson *et al.* (139) suggested that the rate of plant uptake of P was limited by the rate of oxidative phosphorylation within the roots and that the supply of P was quantitatively restricted by the

properties of the external solution. Williams (331) defined parameters of the P status of the soil as:

- (i) capacity factors, which determined the potential supply of P.
- (ii) intensity factors, which determined the strength with which P is held by the soil.
- (iii) rate factors, which are determined by the degree of saturation of the soil with P, the rate of release of P by the soil, the rate of diffusion of P from within reserves, and the rate of plant uptake.

Barber (19) stated that diffusion was the dominant factor controlling P availability, and Hagen and Hopkins (116) attributed decreases in P uptake by excised barley roots with increasing pH to increases in the concentration of divalent P species. Place et al. (231) found maximum availability of P at pH 5.1, and noted that pH affected diffusion particularly in kaolinite systems. Water soluble P was highly correlated with the diffusion coefficient, but pH > 5.6 and the presence of Fe-P decreased the diffusion coefficient. Phillips et al. (229) reported that the effect of Fe-P was significant only in kaolinite systems, and Peaslee and Phillips (227) found that associating ions influenced P diffusion. Ammonium ions depressed P diffusion more than Ca^{2+} while SO_4^{2-} facilitated diffusion more than Cl^- or NO_3^- . Birch (30) considered the degree of base saturation of the soil important in P availability because at higher base saturation, more P was likely to be in salloid than in colloidal form. Lewis and Quirk (170) observed variations in P diffusion with levels

of P applied. Higher levels of application resulted in greater diffusion. Murruman and Peech (210) concluded that the amount of H_2O -soluble P in the soil was dependent on pH and on the size of the labile pool, rather than on the dissolution of crystalline forms of P.

Gunny and Sutton (113) suggested that the size of the pool of labile P and the rate of root extension were the important factors in plant uptake of P. Lewis and Quirk (172) demonstrated that sorbed P could be utilized by plants, and that plant uptake varied with the rate of P application (171). Gerretsen (105) concluded that insoluble P could be solubilized in the rhizosphere and Dalton *et al.* (70) found that added organic materials enhanced P availability probably because decomposition products complexed Al and Fe. Riley and Barber (254) reported decreased P uptake by soybeans at pH > 4.0, and higher P uptake in presence of NH_4^+ than with NO_3^- . The relative effect of NH_4^+ varied with the rhizosphere pH which they suggested depended on the rate of P adsorption. The rate of release of P by the soil materials, is thus dependent on the form of P in the soil, the degree to which the sorption reaction is reversible, the ionic contents and reaction of the soil solution.

Since P retention tends to result in the formation of relatively insoluble compounds, the solubility of these compounds was thought to be a suitable measure of plant availability of P. Pratt (237) concluded that soil P was most soluble at pH 4.2. Several studies have been reported on the effects of individual cations, salt concentrations, organic matter, and clays on the solubility of soil P. Bradfield *et al.* (42) suggested that the dissociation of H_3PO_4

was facilitated by clays and $\text{Ca}(\text{OH})_2$ so that at pH 7.0, PO_4^{3-} was likely to be the dominant ionic form. Wild (328) noted that Ca^{2+} depressed the solubility of Al-P. Lehr and van Wesemael (164) indicated that the depressing effect of cations on P solubility in soils of pH < 5 was in the order $\text{K}^+ > \text{Mg}^{2+} > \text{Ca}^{2+}$, and that the depression due to any of these cations was independent of pH. In the presence of exchangeable Ca^{2+} the formation of Al-P and Fe-P was not influenced by salt concentration, but Ca-P formation could be superimposed (308). Nye and Bertheux (220) stated that organic matter prevented the precipitation of P by Al and Fe, and Weir and Soper (320) found that about 68% of the P retained by Fe-organic matter complexes was available to plants. Swain (289) cited reports by Apuski on the influence of organic matter on the solubility of soil P. Alkali humates were reported to impede the precipitation of Ca-P at pH 4.2 to 8, while raw humus dissolved P from Ca-P. Humic acids leached P from Al-P and Fe-P (289). Huffman *et al.* (133) described several complex forms of Al-P and Fe-P that could be formed in soils and stated that they all dissolved in water, ultimately yielding Al-P or Fe-P. Minimum solubility of Al-P was considered to be at pH 6.0 (210).

Lindsay and Taylor (174) concluded that plant availability of P was correlated with neither the solubility nor the insolubility of P compounds, but was instead related to the rate of formation of the compounds. Materials which formed slowly, e.g., basic Al-P, were more stable and P in them less available; materials which formed rapidly,

e.g., Ca-P provided the most readily plant available P. Juo and Ellis (145) indicated that colloidal precipitates of Al-P and Fe-P formed rapidly and had more surface area than the crystalline materials. They considered the P in the colloidal precipitates more readily available to plants, and the P supply from such compounds to be controlled by the degree of crystallinity in the order: strengite < varisite << colloidal Fe-P = colloidal Al-P. Taylor et al. (294) found colloidal Al-P and Fe-P to be fairly good sources of P, but that plant uptake from these sources was decreased by incubation. Williams (331) stated that most of the plant available P in soils was adsorbed in non-stoichiometric complexes on Al and Fe of hydrous oxides, humates, and clays, and in easily acid-soluble Ca-P compounds. Al-Abbas and Barber (7) found Fe-P most highly correlated with plant available P, but Halstead (118) and Lucas (178) concluded that Al-P was possibly the most important source of plant available P. Shelton and Coleman (275) suggested that the maintenance of high levels of plant available P for long periods of time depended on the relative proportions of Al-P and Fe-P, and on the rate of conversion of Al-P to Fe-P.

Stelly and Ricaud (285) compared plant availability of P to extractability and obtained best correlations with the Bray #1 extractant. Griffin (111) found this extractant to be most uniformly consistent on several Connecticut soils, but observed that it gave 23% lower P extraction at pH 7.7 than at pH 5.3. Levesque and Schnitzer (168) reported that the Bray #1 extractant removed less P from complexes with Al and Fe-fulvates at higher metal:P ratios.

The most meaningful measure of plant availability of P is plant uptake. Lehr and van Wesemael (165) noted that P uptake by plants was dependent on the pH and on the dominant cation in the soil. Calcium ions reduced P uptake relative to Na^+ . Fox *et al.* (94) showed that maximum plant P uptake varied with soil pH, soil composition, and plant species. Hingston *et al.* (123) suggested that P uptake was influenced by the capacity of excretions from plant roots to desorb P from the soil mass. Wright (333) reported the inhibition of P uptake by Al in the soil.

Graham and Fox (108) established that labile K in highly weathered soils was highly correlated with rainfall. The pool of labile K was small presumably because of the high relative activity of Ca^{2+} and K^+ concentration in plants was about 0.5%. Bartlett and McIntosh (23) considered K availability to be influenced by the degree of K saturation of the soil, but Koch *et al.* (158) reported that the uptake of K and the concentration of K in corn grown on Natal oxisols were not influenced by the K status of the soil. Oliveira *et al.* (222) found that plant availability and uptake of K markedly exceeded exchangeable K contents in some Brazilian soils. Plant uptake amounted to < 22% of the total soil K, and even though the concentration of K in plants was about 0.4%, the ratio plant K uptake:soil exchangeable K, varied from 3.3 to 7.2 in Ultisols, and from 3.8 to 9.5 in Oxisols.

Amelioration of Fertility in Red-yellow Soils

The low level of inherent fertility encountered in red-yellow

soils of the tropics is generally attributed to the low base status and low CEC, high P fixation, high permeability, and low water holding capacity (26, 136, 225, 283).

In discussing some of the red-yellow "upland soils" of the Amazon basin, Sombroek (283) observed that whether under forest or savanna, practically all of the CEC was due to the organic fraction. The base saturation relative to CEC at pH 7.0 (potential CEC) was always less than 40% with an average value of 15% in the A horizon. Low base saturation is associated with high acidity, and methods devised for the amelioration of the inherent fertility status must, of necessity, achieve the correction of acidity and improve the degree of base saturation. Applications of lime have been regarded as the best method of correcting soil acidity and the addition of the appropriate fertilizers has served to increase the base saturation. On red-yellow soils, liming has been found to have adverse effects if pH levels above about 5.5 were produced (51, 178, 246).

Soil acidity and plant growth

Soil acidity has been described by Schwertmann and Jackson (274) in terms of pH ranges of buffering. They indicated that at pH levels lower than 4.0 H_3O^+ was the acid entity encountered, but in the range pH 4.0 to 5.6 ionic Al was the source of acidity. Yuan (340) reported a narrower range, pH 4.3 to 5.4. Beyond pH 5.6 hydroxy-Al compounds were considered to be the source of acidity (274).

The effects of soil acidity, per se, on plant growth have been studied in some detail. Several attempts have been made to isolate

the effects of H_3O^+ from those of Al in its various forms. Hackett (114) reported that the germination of several grass species was not affected by H_3O^+ , but that shoot weight decreased as pH fell from 6.5 to 5.5. Rains et al. (241) suggested that H_3O^+ might have impaired overall nutrient uptake through competition for carrier sites or derangement and/or damage to the absorptive mechanisms. The latter may have been due to suppressed dissociation of weak acids at low pH or to progressive and ultimately irreversible alteration in cell structure and function. The addition of Al to acid media decreased and delayed germination of several grasses (114); at low Al concentrations (< 5 ppm) root weights were increased in some cases, but generally there were decreases in root and shoot weight with increasing Al concentration. Hackett (114) concluded that few grass species were tolerant to both low pH and Al. Vlamis (312) pointed out that when plants were susceptible to low pH (H_3O^+) the effects of Al were difficult to detect. Since, however, the pH of most soils is > 4, it would seem that the effects of acidity which are of practical significance are likely to be due to Al.

The adverse effects of Al have not been completely elucidated, but several possible mechanisms have been suggested. It is apparent that the adverse effects of Al include Al uptake and its consequences on the uptake and translocation of nutrients, induced metabolic disorders, and the adsorption and/or precipitation of Al on root surfaces. The effects of Al are normally expected at pH < 5.6, but Soileau et al. (281) observed Al uptake by cotton plants at pH 6.0 to 6.5, and attributed this to the resolubilization of precipitated $Al(OH)_3$.

in the microenvironment of the root. Rees and Sidrak (245) encountered Al toxicity at pH 7.0 to 8.5 on fly-ash soils. These data suggested that Al might be taken up in several forms. Johnson and Jackson (141) reported the uptake of ionic Al by wheat seedlings and DeKock and Mitchell (78) suggested that chelated Al might be taken up by plants. They contended that the charge on the chelate influenced its uptake, lower charges being associated with easier uptake. After uptake the metal is split off by metabolic processes (??).

The uptake of Al has been shown to increase water absorption, reduce uptake and translocation of Ca (141), and disturb the K/Ca balance within the plant (245). Foy et al. (99) established the occurrence of Al-induced Ca deficiency in some soybean plants by autoradiography, and suggested that this differed from absolute Ca-deficiency in terms of the distribution and chemical form of Ca within the plant. Johnson and Jackson (141) found, however, that precipitated or chelated Al exerted no appreciable influence on the uptake of Ca by wheat roots.

The capacity for uptake and translocation of Al varies with plant type. Ahmad (4) reported greater immobility of Al in roots of maize than in those of the cowpea. Ouellette and Dessureaux (224) observed differences in the amounts of Al translocated in different clones of clover. Jones (142) concluded that the amount of Al within a plant was determined by the nature of the buffer system of that plant.

Immobilization of Al by the roots does not lessen the adverse effects of Al on plant growth. Wright (332) established that the

ratio Al(roots)/Al(tops) was highly correlated with yield of barley even though Al (tops) was virtually constant. Generally, the visual symptoms of Al toxicity are localized in the roots. Inhibition of branching and the development of a brownish discoloration (332) of coralloid or stunted roots (4) are now regarded as distinctive symptoms.

Immobilization of Al in the roots has been described as an accumulation of Al in the protoplasmic nuclei (189), or in the vacuoles (256). In the latter case toxicity is thought to be controlled. The mechanisms of immobilization seem to involve adsorption on exchange sites and/or precipitation on root surfaces. Rorison et al. (257) considered Al toxicity to be due to a surface reaction involving saturation of the exchange sites rather than a process of active absorption occurring in the presence of ionic Al. Greatest effects were believed to occur early in plant growth, when the source of nutrients was being changed from the seed to the soil. Clarkson (59) concluded that Al accumulated in the Donnan free space of the roots and prevented exchange reactions with other cations. The adsorbed Al became firmly bound to the cell wall either by precipitation, outside the plasmalemma, of Al(OH)_3 formed on the hydrolysis of Al(OH)_2^+ at $\text{pH} < 6.7$ (59), or by reaction of Al with -COOH groups causing the crosslinking of pectic materials (60). Lance and Pearson (162) suggested that the plasmalemma was the site of injury, Al causing changes in the structural configuration of the membrane.

The immediate consequence of the immobilization of Al in the roots,

is the restriction of movement of P. Wright (332, 334) reported the inactivation of P by Al on roots in contact with ionic or precipitated Al, and it was later demonstrated that this P was held in inorganic form (335). The inactivation of P creates conditions of P-deficiency in the shoots (242), and meristematic regions of the root (335), and restricts cell division by impairing the synthesis of DNA (263), and the hexose phosphorylation processes (59). Clarkson (60) reported that the molar ratio of H_2PO_4/Al in inactivated form tended to a maximum value of 0.3.

The susceptibility of plants to Al toxicity is known to vary with plant type, species, and variety. Rains et al. (241) found differences in tolerance to Al among grasses. Foy et al. (98) reported that wheat varieties varied in tolerance to Al. Ahmad (4) indicated that maize was more susceptible than cowpea to Al toxicity. The evidence suggests that susceptibility is a genetic trait, and various mechanisms have been proposed. Foy and Brown (97) concluded that Al tolerance was related to the capacity for absorption and utilization of P in the presence of excesses of Al. Jones (142) suggested that the buffer systems of Al tolerant plants contained an excess of organic acids which either caused the precipitation of Al in the root zone or maintained the mobility of Al within the plant. The implied principle of exudation of organic acids was also suggested by Foy et al. (98). They regarded wheat plants which caused greater acidification of the root zone as being more sensitive to Al toxicity. Vose and Randall (314) found better relation of Al tolerance to root CEC than to soil type or geographic origin. They concluded that low root CEC was

associated with tolerance, but this seems to conflict somewhat with the concept that saturation of the exchange sites resulted in marked Al toxicity symptoms (257).

Different forms of Al have been shown to be conducive to Al toxicity and to impaired nutrient utilization. Various attempts have been made at characterization of Al in relation to extractability and relative "activity." Ramulu *et al.* (244) used 0.1N NaOH (100C) and reported the extraction of free Al and some Al from Al-silicates. Levesque and Schnitzer (167) used NaOH varying in concentration from 0.1 to 1.0N and considered Al extracted to be that complexed by organic matter. Tandon (293) extracted Al with N NH₄F at pH 8.2. Several workers (174, 190, 218) used N KCl at pH 5.7 to remove exchangeable Al and others adjusted the pH to 2.0 (238, 244). Yuan (342, 345) used N NH₄OAc at pH 4.0 and 4.8, and 0.1N HCl, while Tweneboah *et al.* (301) used 0.1M CaCl₂ (pH 1.5) to estimate "active" Al.

Lin and Coleman (173), and Coleman and Thomas (65) indicated that red-yellow soils contained large amounts of potential acidity which could not be displaced by N KCl. Pioncke and Corey (230) postulated that the amount of acidic Al in a soil was constant and comprised exchangeable and non-exchangeable forms in equilibrium with each other. The amount of extractable Al was reported to vary with vegetation (337) and with soil type (342). Richburg and Adams (252) concluded that the solubility of Al(OH)₃ varied with soil type and with the nature of the Al-polymers present. The polymers may have condensed on solid surfaces (240) or formed part of complexes with organic matter (159).

Nye *et al.* (218) suggested that the concentration of Al in the soil solution would be low if the soil solution had a low electrolyte concentration and the degree of Al saturation was < 60%. At a given pH increasing fertilizer applications increased the Al concentration in the soil solution (51), particularly at pH < 5.8 (191), while increasing organic matter decreased the Al concentration (87). Ragland and Coleman (239) found that exchangeable Al varied with drainage conditions. The relationship between exchangeable Al and pH was described as hyperbolic by Popenoe (234) and by Burgos (51), but Hutchinson and Hunter (135) obtained a linear relationship in surface soils and a curvilinear relationship in subsoils.

Correction of Acidity on Red-yellow Soils

Observing the destructive effects of the continual loss of bases and the concomitant development of acidity in soils comprised largely of 2:1 clays, Joffe (140) suggested that the application of lime would provide a measure of prevention of these effects. Liming such soils satisfied the high Ca requirement of the clay mineral as shown by Snyder *et al.* (280), and stabilized the high humic acid content of the soils by the precipitation of Ca-humates (159). In addition, liming provided a continuous supply of Ca^{2+} to the soil solution which in such soils tends to be at a lower pH than the solid phase, according to Wiklander and Ghosh (326).

When a similar rationale is applied to red-yellow soils, expected results are not realized. Sherman and Fujimoto (276) warned that applications of lime to some Hawaiian soils needed to be carefully

limited. Shuffelen and Middleburg (273) observed that whereas small quantities of lime decreased the permeability of lateritic soils, larger quantities increased it. They interpreted this in terms of competition between the peptizing effect of OH^- and the coagulating effect of Ca^{2+} . Ignatieff and Lemos (136) in reviewing the effects of lime applications to latosols attributed adverse effects partially to the displacement by Ca^{2+} and leaching out of the root zone of K^+ , Mg^{2+} , and micronutrients, and to reduced availability of Fe and Zn at high pH. Sombroek (283) suggested that liming results in decreased availability of plant nutrients, but Reeve and Sumner (246) concluded that induced P fixation was responsible for reduced yields. Fox et al. (94) noted that the effects of lime varied with the soil, but reported appreciable reductions in yield at higher liming rates, as did Burgos (51), Monteith and Sherman (202), Lucas (178), and Reeve and Sumner (246).

Studies aimed at providing a substitute for lime have not been very helpful except for sugar cane (95). Monteith and Sherman (202) used calcium silicate and found that at comparable rates of application, yield depressions were smaller than with lime. Reeve and Sumner (246) attributed a similar difference to the fact that calcium silicate was less soluble and had a lime equivalent value of about 0.30.

Since the supply of Ca in the soil solution of kaolinitic soils is much greater than in montmorillonitic soils (84, 199) and the soil solution in the former soils tends to be higher in pH than the solid phase (326), it would appear that the adverse effects of liming point to the need for a reassessment of the criteria employed in

correcting acidity in red-yellow soils. Indeed, several criteria have been suggested. Coleman *et al.* (63) concluded that N KCl exchangeable Al would constitute a suitable criterion. This was supported by Reeve and Sumner (247), but several modifications have been offered. Sombroek (283) stressed the need for the neutralization of exchangeable Al and the correction of Mn toxicity. Kamprath (147) found that a correction factor of 1.5 or 2 was desirable if exchangeable Al was to be used in this context and pointed out that Ca and Mg should be supplied in addition to the neutralization of exchangeable Al. Vincente-Chandler (311) reported that reduction of exchangeable Al to levels less than 2 meq/100g was optimal. Hoyt and Nyborg (128) suggested that extractable Al would be a valuable supplement to pH in assessing the need for liming.

The reduction of exchangeable Al as a criterion for liming is supported by the findings of McLean *et al.* (190) that lime reacted rapidly with exchangeable Al and only slowly with non-exchangeable Al. The possibilities that these soils are Al-buffer systems (138); that plant growth is limited by exchangeable Al rather than Ca deficiency (87, 100, 147); and that the P status of the soil is influenced by sorption on sesquioxides (276) are all likely to support the adoption of this criterion.

The use of the degree of base saturation as a criterion has also been advocated. Abruna-Rodriguez *et al.* (1) found 60% base saturation or $< 10\%$ Al saturation optimal. Kamprath (147) suggested that $< 15\%$ Al saturation was desirable, and Hutchinson and Hunter (135) indicated that lime applications would be beneficial if Al saturation was $> 25\%$.

The two criteria have exchangeable Al as the common factor and differ markedly in philosophy from the fractional neutralization of titratable acidity. Optimum response to liming was obtained on some red-yellow soils on the Black Sea Coast, when 25% of the titratable acidity was neutralized (82).

Ayres et al. (16) showed that exchangeable Al was reduced to zero at pH 5.0 to 8.4, and Yuan (341) reported that Al was neutralized at pH < 5.4. Burgos (51), however, found that although liming reduced exchangeable Al, uptake of Al by millet was increased. Moschler et al. (205) also obtained reduction of exchangeable Al on liming and in addition reported the reduction of exchangeable K and improved metabolism of N by alfalfa. Koch et al. (158) noted a reduction in the availability of K to corn on Natal Oxisols. The expected increase in exchangeable Ca and CEC of soils were not realized by liming in some cases. Rixon and Sherman (255) could find no significant change in CEC attributable to liming, while Mahilum et al. (179) reported that beyond the first increment of lime, Ca was easily leached.

An alternative approach to the amelioration of fertility in red-yellow soils appears to be the use of P, with Ca supplied only to satisfy plant requirements. Increases in yield on P application in the absence of lime have been reported by Lucas (178), and Plucknett and Sherman (232). Younge and Plucknett (338) advocated the use of P in adequate quantities for the quenching of the fixation capacity of the soil. Several desirable effects on the soil have been attributed to the use of P. Ayres and Hagihara (15) reported the

increased retention of K. Rixon and Sherman (255) pointed out that the effects of P varied with the soil, but obtained increased CEC and exchangeable Ca on some Hawaiian latosols. Plucknett and Sherman (232) also obtained increased CEC and pH on P application to some bauxitic soils of Hawaii. Russell (260) attributed increases in organic matter and N to the use of superphosphate, and noted that for each 1.0% increase in soil N there was a 3.5 meq/100g increase in CEC (262). Increases in N were regarded as the consequence of enhanced N fixation in the presence of added P. Donald and Williams (81) concluded that increases in soil N were directly related to the amount of superphosphate applied. They observed a drop in soil pH, and regarded this as being due to increased CEC concomitant with the build-up of organic matter. Williams and Donald (329) reported that this build up of organic matter permitted the maintenance of constant ratios of C:N:S:P at about 155:10:1.4:1.68, and that S was the limiting factor in the build up of organic matter. Barrow (21) doubted that the accumulation of organic P as noted by Russell (261) would provide a large enough reservoir for plant growth.

The use of P as a means of soil amelioration permits the accumulation of soil organic matter, largely through its positive effect on plant growth, but the rate of accumulation would depend on the ecological conditions prevailing (219), and on the composition of the soil mass.

Indicator CropsPangolagrass

The botanical characteristics of pangolagrass (Digitaria decumbens Stent) were described by Hodges et al. (126). The plant required the maintenance of fertility in the soil for proper growth (124). Gammon (103) found that pangolagrass had a very high K requirement, but that more than 60% of this could be substituted by Na without appreciable reduction in growth. This grass is very sensitive to Ca-deficiency (124), but responds markedly to P (125, 35, 178). Ahmad et al. (6) did not, however, obtain a significant response in P content or yield on Trinidad soils. Phosphorus availability was seen to influence the response of pangolagrass to Ca (127), but Lucas (178) detected no interaction between Ca and P. Hodges et al. (126) stated that pangolagrass could make vigorous growth at pH 4.2 to 4.5 if all the required nutrients were in adequate supply, but that additions of lime improved growth through increased Mg supply and increased efficiency of nutrient utilization. They considered pH 5.5 to be desirable on the acid flatwood soils of Florida (125), but Hortenstine and Blue (127) found pH 6.3 to be optimal on Puletan loamy sand. Liming to higher pH levels depressed yield. Lucas (178) also obtained depressions in yield of pangolagrass on liming an amorphous Costa Rican Entisol from Los Diamantes.

Blue et al. (34) observed slow establishment of pangolagrass on newly cleared land in Costa Rica, but subsequently noted appreciable response to N fertilizers in terms of yield and N concentration in

the tissues. Ahmad et al. (5) also obtained significant responses in yield and N concentration on Trinidad soils.

The selection of pangolagrass as an indicator crop appears justified by the fact that though this species has been "the improved pasture grass" at Ebini for most of the 1960s, its growth and production were, according to Mayers (186), far from satisfactory.

Pigeon pea

Whyte et al. (323) described the botanical characteristics of the pigeon pea (Cajanus cajan (L) Druce). The variety "Norman" which was used in this study was developed from an introduction from Pakistan. It has shown some adaptation to mechanical harvesting and is now being tested in Florida by Killinger (154).

The nutrient requirements of this crop have not been widely studied so far. Krauss (160) concluded that pH 5 to 7 was most favorable, but Lucas (178) obtained no significant response to lime up to pH 6.8. Phosphorus applications gave significant increases in yield. Nichols (211) indicated desirable levels of concentration in the tissues for the major plant nutrients as well as effects of likely interactions and deficiencies (212).

It is not now known whether any attempts at growing the pigeon pea have been made at Ebini, but Mayers (186) reports that the legumes found in that area, e.g., Desmodium advena, Zornia diphylla, did not thrive when incorporated into "improved pastures." The importance of the legume in soil fertility was discussed by Ellison (85), and its more specific role in pastures was examined by Bryan (50). Since,

however, both the capacity of the legume to supply N to the sward and the content of N in its tissues are determined by the amount of N fixation, the focal point in this context is possibly the effectiveness of the symbiotic relationship in which the legume participates, rather than the legume itself. The pigeon pea, therefore, offers a means of assessing the conditions which may have contributed to the failure of those legumes already used.

Vincent (310) reviewed the literature on the environmental factors which are likely to influence N fixation by the legume/Rhizobium symbiosis. He stated that though acidity is generally accepted as the factor of major impact, the broad spectrum Rhizobium japonicum is capable of withstanding pH ≤ 3.5 . Indeed, while the effect of acidity, per se, is more marked in relation to the bacteria than to the host plant (12) nutritional factors normally associated with acidity may affect both symbionts. Inadequate supplies of Ca and Mo, and excessive amounts of Mn and Al are normally associated with acidity. Hallsworth (117) found that liming benefited nodulation when Ca supply in the soil was low, but Andrew and Norris (13) showed that tropical legumes were capable of nodulating in conditions of Ca-deficiency. The tropical legumes vary in their response to added Ca because of inherent differences in their capacities for extracting Ca from soil (13). It has been shown that the Rhizobium has lower requirements for Ca than for Mg (215, 309), but Vincent (310) cautioned that the need may be for divalent cations rather than for Ca or Mg specifically. Norris (216) classified Rhizobium strains normally associated with legumes adapted to acid soils, as alkali producers. This may be of

considerable importance to the nutrition of the host plant.

Dobereiner (80) attributed responses to Ca by beans, to control of the Ca/Mn ratio in the plant, while Foy *et al.* (99) distinguished between absolute Ca deficiency and Al-induced deficiency observed in different varieties of soybean. Ouellette and Dessureaux (224) considered that the rate of Ca uptake was the important factor in tolerance to Al and Mn by different legumes. The more tolerant types had the highest Ca contents. Henzell (121) indicated that differences in the capacity of legumes to extract Ca from the soil were genetic in origin, and that similar differences existed in capacities for extraction of Ca and P, and in tolerances to excesses of Al and Mn.

The importance of P to the legume was stressed by Van Schreven (305), and Vincent (310) observed that deficient P supplies to the host plant had indirect adverse effects on both the formation and functioning of nodules. Dobereiner (80) noted that P stimulated N fixation but did not counteract excesses of Mn.

It would seem that though the primary purpose of cultivation of the legume is N fixation, this purpose is likely to be defeated in a soil which contains appreciable quantities of combined N. Stewart (287) stated that such conditions resulted in the decrease of the number of root infections by Rhizobium, and in the number and importance to the host plant of those nodules which developed. Whether those nodules which develop are effective or not, is dependent on the development of hemoglobin in the nodule (217).

MATERIALS AND METHODS

Soils

Samples of four soils which occur on the White sand plateau were taken by members of the staff of the Ministry of Agriculture, Guyana, and shipped in an air-dry state to Miami, Florida. The samples were quarantined and fumigated at the port of Miami, then transported to Gainesville, where they were screened (5 mm), air-dried, and stored in polyethylene bags.

The soils were described by Brinkman (45) as follows:-

- I. Ebini sandy loam - a well-drained soil intergrading from a red-yellow latosol to a red-yellow podzol (Typic normochrult) developed in fine-textured sediments of the Berbice formation under forest and savanna vegetation. This soil occurs often on the lower parts of slopes where residual material from crystalline rocks and unconsolidated colluvium are present. It correlates well with similar soils of the Brazilian states of Sao Paulo and Rio de Janeiro, and is usually associated in the Ebini area with the coarser-textured Kasarama loamy sand and Takama sand (45).
- II. Kasarama loamy sand - a well-drained red-yellow latosol (Ochric ustox), developed in medium-textured sediments under forest and savanna vegetation. It occurs on gentle slopes, and like the Ebini sandy loam may have numerous anthills

when under savanna vegetation. This soil is intermediate in texture between the Ebini sandy loam and the Tabela sand with which it may be associated (45).

III. Tabela sand - an excessively drained regosol (Ultic quartzipsamment) developed in sandy sediments under forest and savanna vegetation. It occurs on undulating or gently sloping relief in association with Kasarama loamy sand, Takama sand, and Tiwiwid sand. It is coarser-textured than the Kasarama and Takama soils and browner in color throughout than the Tiwiwid sand (45).

IV. Tiwiwid sand - an excessively drained regosol (Typic quartzipsamment), developed under forest and scrub-tree vegetation in coarser-textured sediments. It occurs in relatively large areas in higher portions of the landscape and in colluvial positions on creek slopes in association with Ituni sand, Tabela sand, and Kasarama loamy sand (45).

Samples of the Tiwiwid sand were taken from the surface horizon only. The remaining samples embraced the four uppermost horizons.

Soil Analysis

Particle-size analysis was effected by the method described by Day (72) using 20-g oven-dried (105C) samples and omitting the filtration process.

Samples for mineralogical analysis were pretreated according to the techniques detailed by Kunze (161). Sub-samples were prepared by

the methods of Whittig (322), and examined for X-ray diffraction patterns as oriented aggregates on a glass slide. X-rays emanated from a Cu-source and were passed through a Ni filter and a 3° beam slit. A proportional counter with a voltage of 1,500 V served as the detector with a detector slit of 0.05° . Samples were scanned over the range of 2θ values from 2° to 40° at a speed of $2^{\circ}/\text{min}$. Sub-samples of the pre-treated soils saturated with Mg were used for differential thermal analysis over the temperature range 50 to 1,100°C at a heating rate of 10°C/min. using a soil:burnt asbestos ratio of 1:3 (22). Further sub-samples were saturated, mounted and shadowed as directed by Kittrick (155), examined under a Phillips E M 100 B electron microscope, and photographed.

Amorphous materials were extracted from the soils by a citrate-bicarbonate-dithionite solution buffered at pH 8.5 (161). Each 10-g soil sample was extracted four times, and the supernatant solutions were made to volume and analysed for Al, Fe, Si, and Mg using a model 303 Perkin-Elmer atomic absorption spectrophotometer.

Organic matter contents were determined by weight loss on heating 20-g oven-dried (105°C) samples at 375°C for 16 hours as described by Ball (18). Organic C was studied by the Walkley-Black method of wet oxidation outlined by Allison (11). Organic matter was extracted with 0.5N NaOH (203), and precipitated according to Yuan's method (341).

The total contents of various elements in the soils were measured by the HF-HClO₄ method of Jackson (137). Soil digests were analyzed for Al, Fe, Ca, and Mg by atomic absorption spectrophotometry and for

K by flame emission. Total N was determined by micro-Kjeldahl with the salicylic acid modification of Volk and Fontein.¹ Total P was measured by the chlorostannous-reduced molybdophosphoric blue color method in a HCl system as directed by Jackson (137).

Cation exchange capacity determinations were made using N NH₄OAc (pH 7.0) and N KCl (pH 5.7) as saturating solutions. The NH₄⁺ was displaced by N NaCl (pH 2.5) as suggested by Chapman (57) and measured by distillation while K⁺ was displaced by N CaCl₂ and measured by flame emission after the method of Bhumbra and McLean (29).

Exchangeable bases Ca, Mg, and K were determined in the N NH₄OAc leachate, while Al, Mg, and Ca were measured in the N KCl leachate. Exchange acidity was found by titration of the BaCl₂-TEA extract with dilute HCl, using a mixed bromocresol green-methyl red indicator as recommended by Peech (228). Titration curves were constructed from pH values after addition of known amounts of HCl or KOH to 5-g soil samples in 50 ml N KCl as described by Puri and Swarnakar (238).

A Corning Model 12 glass-electrode pH meter was used to determine the soil pH in a 1:1 (^{w/v}) soil-water suspension and 1:2.5 (^{w/v}) soil N KCl suspension.

Moisture equivalents were estimated by the method of Briggs and McLane (44).

¹ Unpublished mimeographed sheet. Department of Soils, Univ. of Florida, Gainesville.

Plant Analysis

One-gram samples of oven-dried (70C) plant tissues were ashed in a muffle-furnace at 425C for 12 hours. On cooling, 5 ml of N HNO_3 were added to the ash and evaporated to dryness on a hot plate at 90C. The dried samples were then heated to 425C for 2 hours and taken up in 2 ml N HCl . This is essentially Peech's technique as described by Jackson (137). The solutions were filtered into 100 ml volumetric flasks, and made up to volume with deionized water. Five-milliliter aliquots were used for the determination of P by the 1,2,4-aminonaphthol-sulfonic acid-reduced molybdatephosphoric blue method of Fiske and Subbarow (91). Calcium, Mg, Fe, Zn, Mn, and Cu in the solutions were determined by atomic absorption spectrophotometry and K by flame emission. Nitrogen was determined in 0.20-g samples of oven-dried (70C) material by the micro-Kjeldahl method with the salicylic acid modification of Volk and Fontein.¹

Results of the analyses were computed on the oven-dry (70C) basis.

Laboratory Experiments

Experiment 1. Incubation Studies

Five hundred gram samples of the surface horizons of the soils were incubated with various levels of P at different pH levels. Initially 2 kg samples of each soil were mixed in the air-dry state with the levels of CaCO_3 required to produce pH (N KCl) levels of 5.5, 6.0, and 7.0 respectively. These samples were divided into 500-g

portions which were then moistened with distilled water to field capacity and incubated under laboratory conditions for 2 weeks. Distilled water was added as required to maintain each sample at constant weight over the period of incubation. The pH (N KCl) level of each sample was recorded after 2 weeks of incubation and P added at levels of 0, 50, 100, and 150 ppm, to randomly selected samples to give the effect of a 4 x 4 factorial design. The CaCO₃ treatments were, however, not orthogonal. The source of P was KH₂PO₄, and this was added with other nutrients to provide final levels of N (100 ppm, from NH₄NO₃), K (100 ppm, from KH₂PO₄ and KCl), Mg (40 ppm, from Mg(OAc)₂, and MgSO₄), S (20 ppm, from MgSO₄), and micronutrients from FTE 504² at 30 kg/ha.

The samples were then adjusted to field capacity with distilled water, covered and left thus for 12 weeks. Thereafter, they were allowed to attain an air-dry state and stored for subsequent analysis. Subsamples were used for:-

- i. Leaching studies.--Ten-gram samples from each treatment were weighed in duplicate into "leaching tubes" and leached with 200 ml distilled water. No attempts were made to minimize the disturbance of the soil, but the head of water in the tubes was kept at a maximum of 20 cm. The leachates were collected and analysed for Ca and Mg by atomic absorption spectrophotometry, for K by flame emission, and for

² FTE 504 contains 4.00% B, 7.00% Cu, 14.00% Fe, 7.00% Mn, 7.00% Zn, and 0.07% Mo.

P by the chlorostannous-reduced molybdophosphoric blue method in an HCl system (136).

ii. Exchangeable cations.--Ten-gram samples from each treatment were weighed in duplicate into 100 ml polyethylene centrifuge tubes and shaken with 50 ml of $\text{N NH}_4\text{OAc}$ (pH 7.0) for 1 hour on a reciprocal mechanical shaker. The tubes were left standing overnight then centrifuged, and the supernatant decanted. The $\text{N NH}_4\text{OAc}$ washing was repeated with 10 min. shaking to give a total of four washings per sample. The supernatant solutions were combined and made up to 200 ml with $\text{N NH}_4\text{OAc}$ (pH 7.0), then analyzed for Ca, Mg, and K by the techniques used in (i) above. Results were corrected for the amounts removed by leaching and categorized as exchangeable nutrients retained against leaching.

iii. Extractable phosphorus.--Two-gram samples from each treatment were weighed in duplicate into 100-ml polyethylene centrifuge tubes and shaken for one min. with 20 ml of a solution of 0.03 $\text{N NH}_4\text{F}$ in 0.025 N HCl , according to Jackson's description of the method of Bray and Kurtz (137). Appropriate aliquots were analysed for P by the technique used in (i) above.

Experiment 2. - Studies on the Organic Fraction of the Soils

Twenty-five gram samples of soil from each horizon were weighed out in duplicate into 100 ml polyethylene centrifuge tubes and shaken for 1 hour with 50 ml 0.5 N NaOH on a reciprocating mechanical shaker.

The tubes were left standing overnight then centrifuged and the

supernatant solution decanted. This 0.5N NaOH extraction was repeated and the supernatant solutions from each extraction of each horizon combined and adjusted to a final volume of 200 ml with 0.5N NaOH. Ten-milliter aliquots from each extract of organic matter were put in 100 ml beakers and adjusted with 2N H₂SO₄ to pH values of 1, 2, 3, 10. They were then transferred to 100 ml centrifuge tubes with all washings and centrifuged. The supernatant solutions were decanted into 100 ml beakers and evaporated to dryness on a hot plate at 80°C, then heated to 450°C for 2 hours to oxidize all the carbon. The residues were taken up in 2 ml 5N HCl and filtered into 100 ml volumetric flasks, made up to volume with distilled water, and analysed by atomic absorption for Al and Fe. Ten milliter aliquots of the 0.5N NaOH extracts at pH 12.2 were also evaporated to dryness, ashed at 450°C, and analysed as above for Al, Fe, Ca, Mg, and Mn, and by flame emission for K. The precipitates formed on acidification of the NaOH extracts and 10 ml aliquots of the original extracts were analysed for C content by the Walkley-Black method (11). Appropriate aliquots of the NaOH extracts were used for determination of N and P by the respective methods indicated above.

Absorption spectra were constructed by the method described by Yuan (341, 343) using aliquots of the original NaOH extracts which had been adjusted in volume to provide equal concentrations of C.

Greenhouse ExperimentsExperiment 1. - Limiting Nutrients Study

Two-kilogram samples of soil from each of the surface horizons were adjusted to pH 6.0 by the addition of CaCO_3 on the basis of previously constructed titration curves. The samples were then kept in a moist condition for 2 weeks in plastic pots. On the basis of a randomly assigned 2^5 factorial treatment plan, P (100 ppm) as KH_2PO_4 , K (100 ppm) as KCl , S (20 ppm) as MgSO_4 or N (100 ppm) as NH_4NO_3 , and micronutrients as FTE 504 at a rate equivalent to 30 kg/ha, were added to appropriate pots. Magnesium was added as $\text{Mg}(\text{OAc})_2$ to give a final level of 40 ppm in each pot.

Complete 2^5 factorial studies were run on each surface soil using pangolagrass, and on each soil except the Ebini sandy loam using pigeon pea. Rooted pangolagrass cuttings were planted in appropriate pots on November 3, 1969, and harvested 10 weeks later on January 17, 1970. A second harvest was taken on March 15, 1970, after which the soils were allowed to dry. The roots were then removed, washed thoroughly, and dried at 70C. Pigeon pea seeds inoculated with a broad spectrum Rhizobium strain were planted in appropriate pots on December, 3, 1969, and harvested 12 weeks later on February 22, 1970. The roots were removed immediately after harvesting of the tops and examined for nodule development, washed thoroughly, and dried. All harvested material was appropriately labelled and weighed after drying at 70C. Neither study was replicated.

Experiment 2. - Optimum Levels of Ca, P, and K

On the basis of data gleaned from Experiment 1, a central orthogonal composite design described by Mendenhall (201) was used to determine the levels of Ca, P, and K which were required for maximum plant growth.

Each category of soil from the previous greenhouse study was combined with unused samples from the same horizon; FTE 504 was added at the rate of 7.5 kg/ha, and the whole sample thus obtained thoroughly mixed. The pH (H_2O) value of the soil from each surface horizon were then measured. The total quantities of CaCO_3 necessary to satisfy the requirements of the design were then thoroughly mixed with suitable quantities of each soil.

Limed and unlimed soils from each surface soil were thoroughly mixed in proportions calculated to give the finally desired levels of Ca and pH in each treatment. Two-kilogram samples were then put into plastic pots and kept in a moist state in the greenhouse for 2 weeks, after which appropriate quantities of P (as KH_2PO_4 and $\text{NH}_4\text{H}_2\text{PO}_4$), and K (as KCl and KH_2PO_4) were added to the pots. Other nutrients were also added at this time including N (100 ppm) as $\text{NH}_4\text{H}_2\text{PO}_4$ and NH_4NO_3 , S (20 ppm) as MgSO_4 , Mg (40 ppm) as $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Mg}(\text{OAc})_2$, B (5 ppm) and H_3BO_3 , Mo (5 ppm) as $(\text{NH}_4)_6\text{Mo}_7\text{O}_24 \cdot 4\text{H}_2\text{O}$.

Rooted sprigs of pangolagrass were planted (three/pot) on the Tabela sand, the Kasarama loamy sand and the Ebini sandy loam, on July, 1970, and harvested 8 weeks later on September 15, 1970. Urea (100 ppm N) was added to each pot 1 week before harvesting and

a second harvest was taken on December 12, 1970. A similar application of N was made and a third harvest was obtained 8 weeks after the second. The roots were left in the pots until the soil dried then removed, washed thoroughly, dried at 70C, and weighed.

Pigeon pea seeds (five/pot) inoculated with a broad spectrum Rhizobium strain were planted on the Tiwiwid sand and Kasarama loamy sand on July 8, 1970. Nutrients had been added as indicated above, except for the omission of the N sources, $\text{NH}_4\text{H}_2\text{PO}_4$ and NH_4NO_3 .

Tops were harvested on September 26, 1970, and the pots left to dry before the roots were removed and examined. There were three replications in this experiment, as in the pangolagrass study.

The indicator crops were utilized in an attempt to characterize the response surface of each soil for each crop in so far as limitations in quantity of soil permitted. Dillon (79) observed that response surfaces in crop and livestock production can be very well depicted by studies based on central composite designs. Such designs permit a greater number of treatments and are more conducive to accuracy than conventional factorial studies.

The central composite design was developed by Box and Wilson (39) to estimate response functions. The effect of each parameter in the function is reflected by its coefficient. They pointed out that estimates of a coefficient will differ from the true value because of experimental error and because of biases which arise when it is impossible to represent the surface by equations of the type fitted. Nevertheless, it is not recommended that non-significant terms in the fitted equation be dropped, since they provide the best

estimate of any given effect from the available data. Hader *et al.* (115) stated that when the variance of the estimated coefficient was used as a criterion, the central composite design was more efficient than a comparable complete factorial.

Box and Youle (40) indicated that the general shape of the response surface and of the area of the maximum were determined by the presence or absence of interaction among the variables. In the presence of interaction a ridge rather than a point corresponded to the maximum, which could be attained by several different combinations of the interacting variables. The existence of interaction amongst plant nutrients is known (279) as are the additional influences of season (302), and rainfall (339). This design permits a closer examination of more variables, and the values at which they combine to provide a maximum, could be computed from the fitted equation as discussed by Box (38).

The use of a central composite design has limitations in that the variance of the response is not uniform over the experimental region, but increases with increasing distance from the center of the region (201). This introduces an element of tedium to multi-parameter inference making procedures.

RESULTS AND DISCUSSION

Profile Characterization

Particle-size Analysis

In each profile the proportions of clay and silt increased with depth, while those of sand decreased, as shown in Table 1. The increase in silt content appeared, except in the Kasarama loamy sand, to be largely in the 0.005 to 0.02 mm particle-size range, while the decrease in sand content was most marked in the medium sand (0.10 to 0.50 mm) fraction. The proportions of very fine sand (0.00 to 0.10 mm) increased continuously down the profile while those of coarse and very coarse sand increased to a maximum and then decreased again. The increase in relative amounts of particles of smaller size with depth appeared to be a result of the movement of water down the profile and the consequent segregation of smaller particles as structural aggregates were modified (298). While the proportions of inorganic particles of colloidal size increased with depth, organic colloids decreased appreciably though there was a small increase seen in the B_{21} over the B_1 horizon of the Kasarama loamy sand, and in the C over the B_3 of the Ebini sandy loam. These increases may not be significant, but the cessation of the decreasing trend was perhaps due to a reduction in rate of movement of percolating water as the

Table 1.—Particle size distribution in the soils.

water table was approached, and possibly to the saturation of the organic colloids by hydrous oxides.

Clay Fraction

The X-ray diffraction patterns of the clay fractions from the Ebini profile shown in Fig. 1 were virtually identical to those obtained for clay fractions from the other soils, regardless of whether the samples were Mg-saturated and glycerol-solvated, or K-saturated and air-dried. The diffraction peaks occurred at 2θ values of 10.5° to 11° , 22.7° to 33° , and 35.5° to 38° , corresponding to first-, second-, and third-order diffractions, respectively. These peaks indicated a diffraction spacing of approximately 7.1 to 8.5 \AA° , suggesting the presence of kaolinite, metahalloysite, and/or chlorite (322). All the diffraction patterns obtained after heating the K-saturated samples to 500C for 2 hours were similar to those shown in Fig. 2. The disappearance of the peaks on heating indicated that kaolinite was the clay mineral in the samples. This was confirmed by electron microscopy. The micrographs a - d shown in Fig. 3 were probably not representative of the degrees of crystal imperfection to be expected in a given soil, but reflected the various stages of degradation of the clay crystals that might be encountered. Further evidence of the kaolinitic nature of the soil clays was provided by differential thermal analysis. The DTA traces shown in Fig. 4 were typical of those obtained for all samples. The endothermic peaks at 580C were probably due to the loss of water in the crystal lattices and the breakdown of crystal structures, while

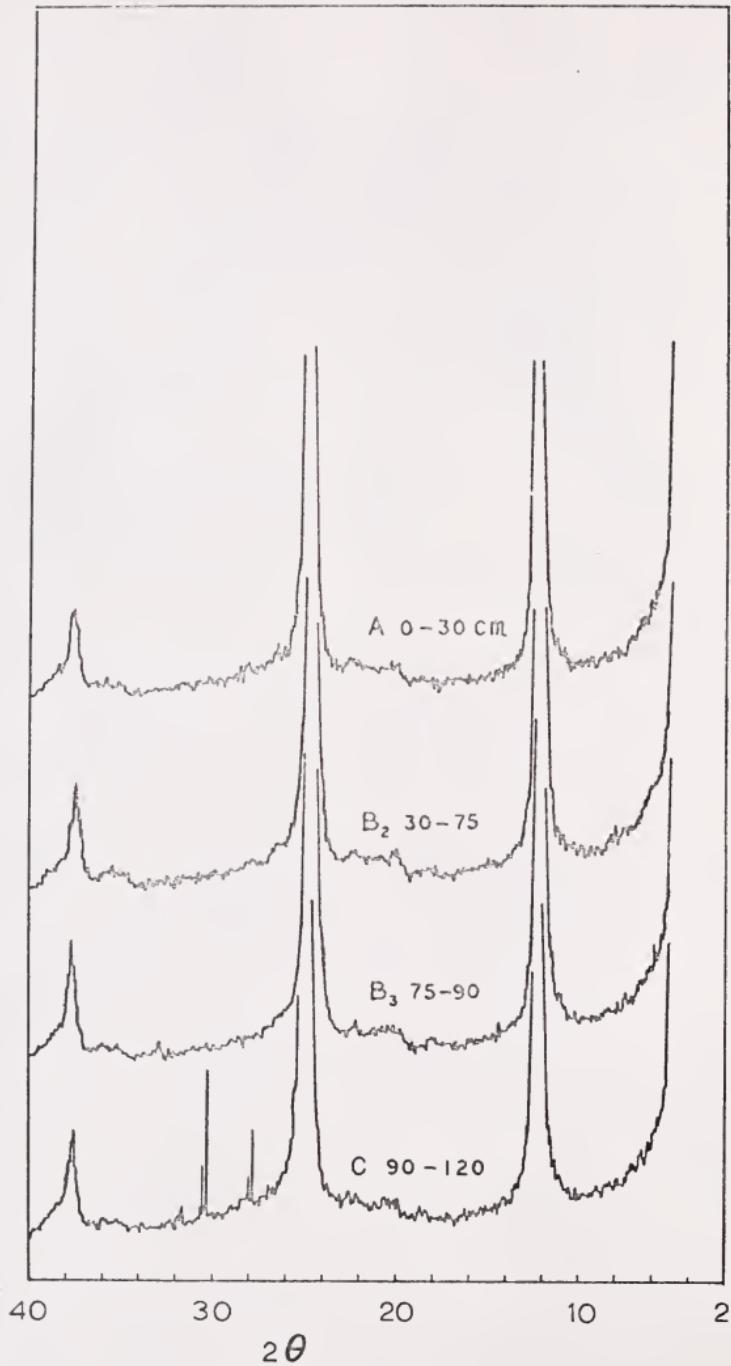


Fig. 1. -X-ray diffraction patterns of K-saturated clay from the Ebini sandy loam.

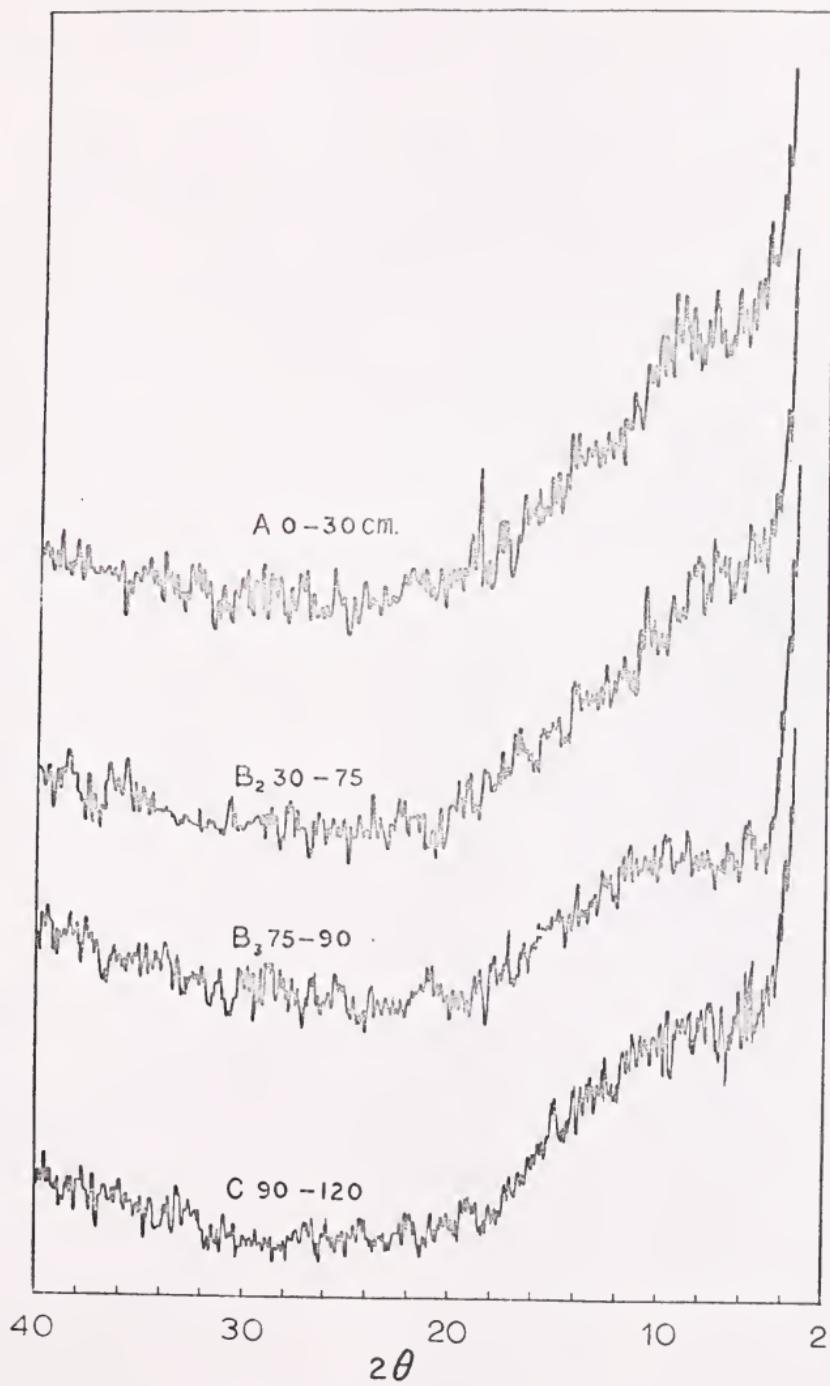
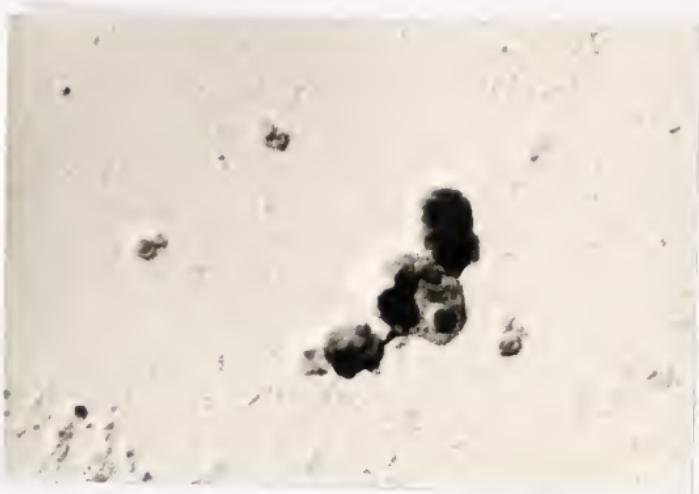


FIG. 2.—X-ray diffraction patterns of heated K-saturated clay from the Ebini sandy loam.



(a) Tiwiwid (44,000x)

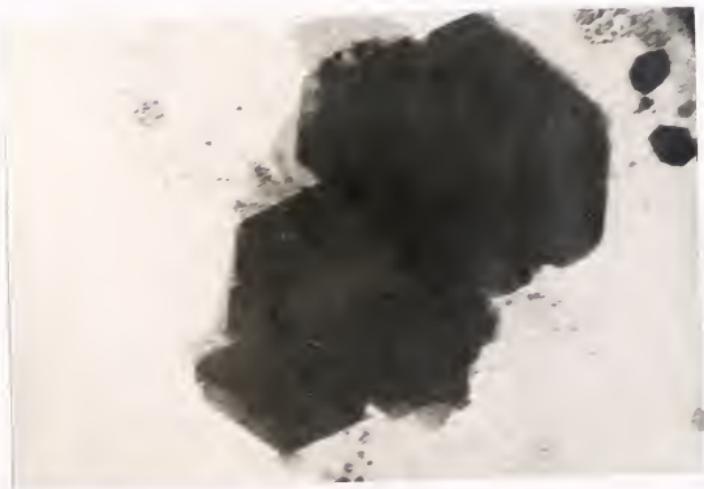


(b) Kasarama (38,000x)

Fig. 3. --Electron micrographs of clay separates from the surface horizons.



(c) Tabela (53,000x)



(d) Ebini (44,000x)

Fig. 3. --Cont'd.

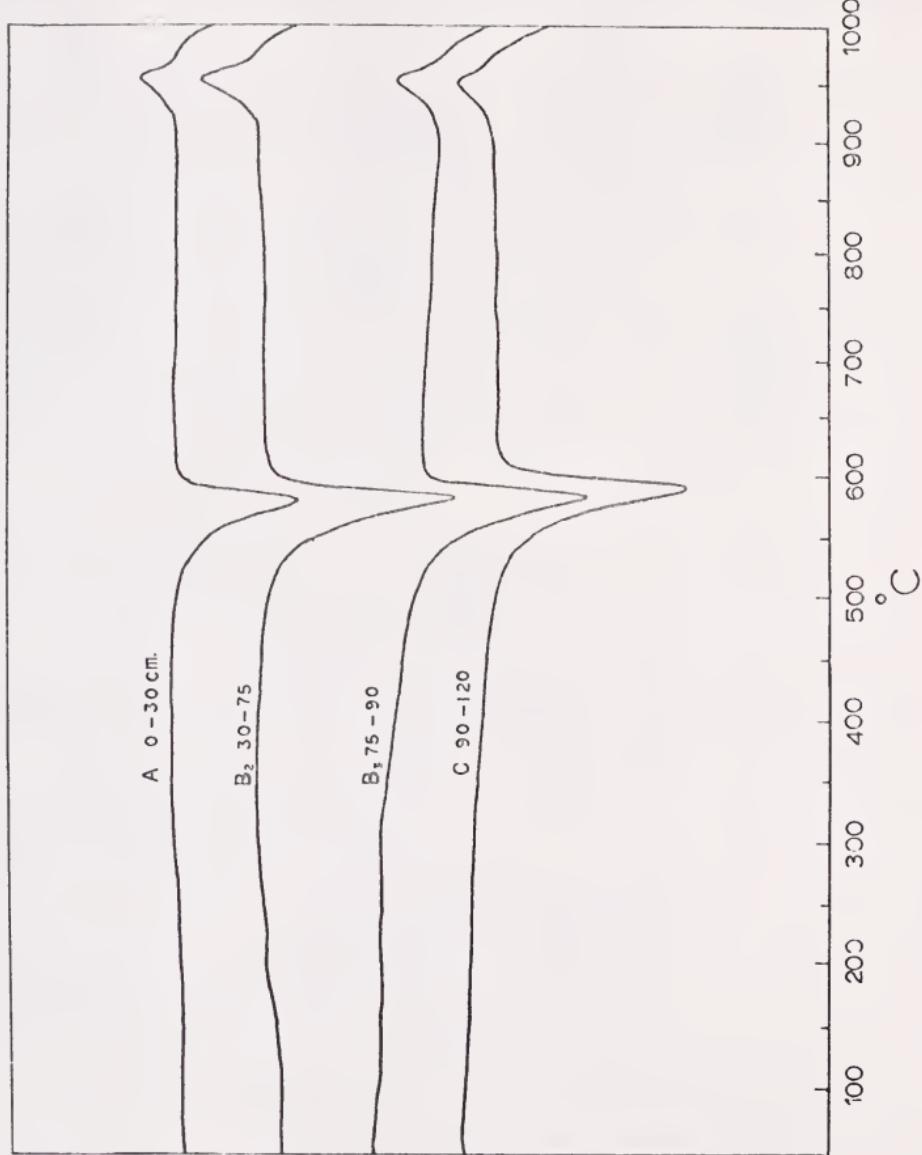


Fig. 4. --Differential thermal analysis traces of Mg-saturated clay of the Ebini sandy loam.

the exothermic peaks at 1,050°C were indicative of the crystallization of corundum, as stated by Mason and Berry (185). The skewed nature of the endothermic peak might have been attributable to the presence of some halloysite (22), but no evidence of halloysite was gleaned by electron microscopy. The poor crystallinity of the kaolinite may, therefore, have been responsible for the character of the peak. The DTA traces demonstrated the absence of any chlorite, gibbsite, goethite, or brucite (22). Gibbsite was also absent from a sandy yellow latosol which had kaolinite as the only clay mineral, and which developed from Quaternary alluvial sediments in the Amazon (52).

The total Al and Fe contents of the clay separates are listed in Table 2. Except for the surface horizons of the Tiwiwid and Tabela sands, and the B₂₁ horizon of the Kasarama soil, the contents of Al did not vary greatly from the value of 20.9% indicated by the chemical formula for kaolinite (185). This suggested that the loss of crystallinity involved approximately equal changes in the contents of Al and Si, rather than a process of desilification (52). The small, but virtually constant content of Fe was probably due to isomorphous substitution (223). It is also possible that some Fe may not have been removed by the citrate-bicarbonate-dithionite extractant (288), but several reports attest to the capacity of the extractant (92, 344) for the complete removal of Fe, and to its greater efficiency in acid than in neutral soils (319). The amounts of amorphous oxides removed by this extractant are

Table 2. --Aluminum and Fe contents of clay separates.

Soil	Horizon and depth cm	Element	
		Al	Fe
Tiwiwid sand	Surface	18.10	1.88
Tabela sand	A ₁ 0 - 20	15.00	0.84
	C ₁ 20 - 50	20.00	1.84
	C ₂ 50 - 90	20.50	1.09
	C ₃ 90 - 120	20.80	1.04
Kasarama loamy sand	A ₁ 0 - 25	21.25	1.18
	A ₃ 25 - 40	20.25	1.11
	B ₁ 40 - 55	20.20	1.16
	B ₁ 55 - 85	24.00	1.15
Ebini sandy loam	A 0 - 30	22.00	1.23
	B ₂ 30 - 75	22.70	1.16
	B ₃ 75 - 90	22.30	1.16
	C ₃ 90 - 120	22.00	1.15

shown in Table 3. From the data it is clear that the clay crystals were not saturated with ferric oxides. The 10 to 12% (w/w) requirement (282) was never met. The relatively large quantities of SiO_2 may have been due partly to the progressive degradation of crystalline clays and partly to its accumulation in association with (319) or occluded by (2) hydrous oxides of Al and Fe. The total contribution to the clay fraction of the soils by the amorphous materials tended to decrease with increases in the depth of the horizon, but was in every case less than 10% (w/w), as postulated for similar soils by Bennema (26).

Organic Fraction

The organic fractions of the different horizons are described quantitatively in Table 4. The decreasing trends with increasing depth of the horizons, revealed by loss of weight on ashing the soils at 375°C, paralleled those of organic C content as measured by the Walkley Black method. The B₂₁ and C horizons of the Kasarama and Ebini soils, respectively, varied somewhat from the general trend. The loss in weight on ashing was greater in these horizons than in those immediately above them. The ratios of weight loss to per cent organic-C increased with increasing depth of the horizon in each soil. In the surface soils, these ratios were consistently lower than the "Van Bennelen factor" of 1.724 (11). This was also true for the C, and A₃ horizons of the Tabela and Kasarama soils, respectively. The factor of 2.5, proposed by Broadbent (46) for subsoils was exceeded in the two lowest horizons of each profile except for the B₁ horizon of the

Table 3. --The composition and distribution of the amorphous material in the soils.

Soil	Horizon and depth	Amorphous materials					Soil (W/W)
		Al ₂ O ₃	Fe ₂ O ₃	SiO ₂	Total	Clay (W/W)	
C.T. UG/G							
Tiwivid sand	Surface	232	43	3,744	4,018	1.3	0.4
Tabela sand	A ₁ 0 - 20	3,307	343	3,744	7,293	9.4	0.7
	C ₁ 20 - 50	4,960	479	4,011	9,449	7.3	0.9
	C ₂ 50 - 90	6,850	654	3,209	10,713	6.6	1.1
	C ₃ 90 - 120	4,724	522	8,557	13,803	8.1	1.4
Kasarama loamy sand	A ₁ 0 - 25	4,015	229	4,546	8,790	6.5	0.9
	A ₂ 25 - 40	3,307	268	3,744	7,218	4.8	0.7
	B ₁ 40 - 55	4,251	375	7,220	11,847	7.5	1.2
	B ₂ 55 - 85	4,015	382	6,952	11,350	5.4	1.1
Ebinini sandy loam	A 0 - 30	3,543	293	6,150	9,986	6.7	1.8
	B ₂ 30 - 75	5,007	361	8,557	13,925	6.3	1.4
	B ₃ 75 - 90	6,141	540	7,755	14,435	5.0	1.4
	C ₃ 70 - 120	6,566	451	8,289	15,317	4.4	1.5

Table 4. --Data on the organic fraction of the soils.

Soil	Horizon and depth cm	Loss (%) at 375C (1)	Organic C (2)		Apparent C in O.M. %	Ratio (1)/(2)
			%	%		
Tiwiwid sand	Surface	2.75	1.75	64		1.57
Tabelia sand	A ₁ 0 - 20	1.06	0.78	73		1.34
	C ₁ 20 - 50	0.96	0.63	66		1.52
	C ₂ 50 - 90	0.82	0.29	35		2.83
	C ₃ 90 - 120	0.64	0.21	23		3.05
Kasarama loamy sand	A ₁ 0 - 25	1.45	0.90	62		1.61
	A ₃ 25 - 40	1.01	0.73	72		1.38
	B ₁ 40 - 55	0.85	0.28	31		2.43
	B ₂ 55 - 85	0.89	0.28	31		3.18
Ebini sandy loam	A 0 - 30	1.80	1.18	66		1.53
	B ₂ 30 - 75	1.01	0.48	48		2.10
	B ₃ 75 - 90	0.94	0.27	29		3.48
	C 90 - 120	1.10	0.25	23		4.40

Kasararama loamy sand.

The disparities between the weight loss:organic C ratios, and the conventional conversion factors could be expected to hinge on the true C content of organic fraction, the relative accuracy of the different methods of measurement, and the existence of definite sources of error. Estimates of the C content of the organic material--apparent C concentration in organic matter--(Table 4), show that the organic fraction of the upper two horizons of the soils had more than 58% C, while those of the lower two horizons and the B₂ of the Rhini soil had much less. Residues of vegetation burnt on the surfaces of the soils may have inflated the estimates for the upper horizons. The extremely low C content of the lower horizons may have been due in part to inflation of the weight changes on ashing by structural water in the inorganic materials (18). As much as 3.8% of the inorganic material may be lost at 375°C (243), and the substantially higher clay contents of the lower horizons could, therefore, have depressed the apparent C concentration in the organic fraction. The efficiency of the wet oxidation process in measuring the organic-C contents is determined to some extent by the chemical complexity of the organic material (11), and by the nature of the bonds by which this material is linked to the inorganic fraction of the soil. The close association of organic material and clay observed in the Tiwiwid sand and the absence of interlayer spaces in the clay point to the likelihood of almost total oxidation of C.

The chemical complexity of the organic fractions was compared by the construction of absorption spectra in the range 450 to 475 μm

using 0.5N NaOH extracts (pH 12.2) from the different horizons, adjusted to similar C concentrations. The absorption spectra are shown in Fig. 5 (a - d). The differences in the slopes of the extracts from the surface horizons, Fig. 5 (a), indicate that the material extracted from the Tiwiwid sand had the highest degree of aromaticity and that from the Tabela sand had the highest proportion of aliphatic C (159). The degree of aromaticity in material extracted from the horizons of the profiles decreased with increasing depth of the horizon, Fig. 5 (b - d), reflecting the presence of increasing proportions of the less aromatic fulvic acids (300) with depth in the profile. This trend is reflected by the humic-C:fulv-C ratios, though in the brown sand soils, the Tabela, Kasara, and Ebini, humic-C was absent from all but the surface horizon (Table 5). The proportion of organic C not extracted by alkali in the soils was greater than 60% in every case, suggesting that there were substantial amounts of humins present. The marked decline, with depth, in C/N ratios of the extracted material in spite of increasing amounts of fulvic acids, was probably due to the movement of inorganic-N down the profile. The wider C/N ratios throughout the Ebini profile perhaps resulted from a poorer supply of inorganic-N in the surface horizon.

An examination of the response of alkali-extracted material to variation in pH showed that there was maximum precipitation of C at pH 1 from the Tiwiwid, and at pH 5 from the brown sand soils (Table 6). The material precipitated from the Tiwiwid extract was completely redissolved at approximately pH 2.8, while that precipitated

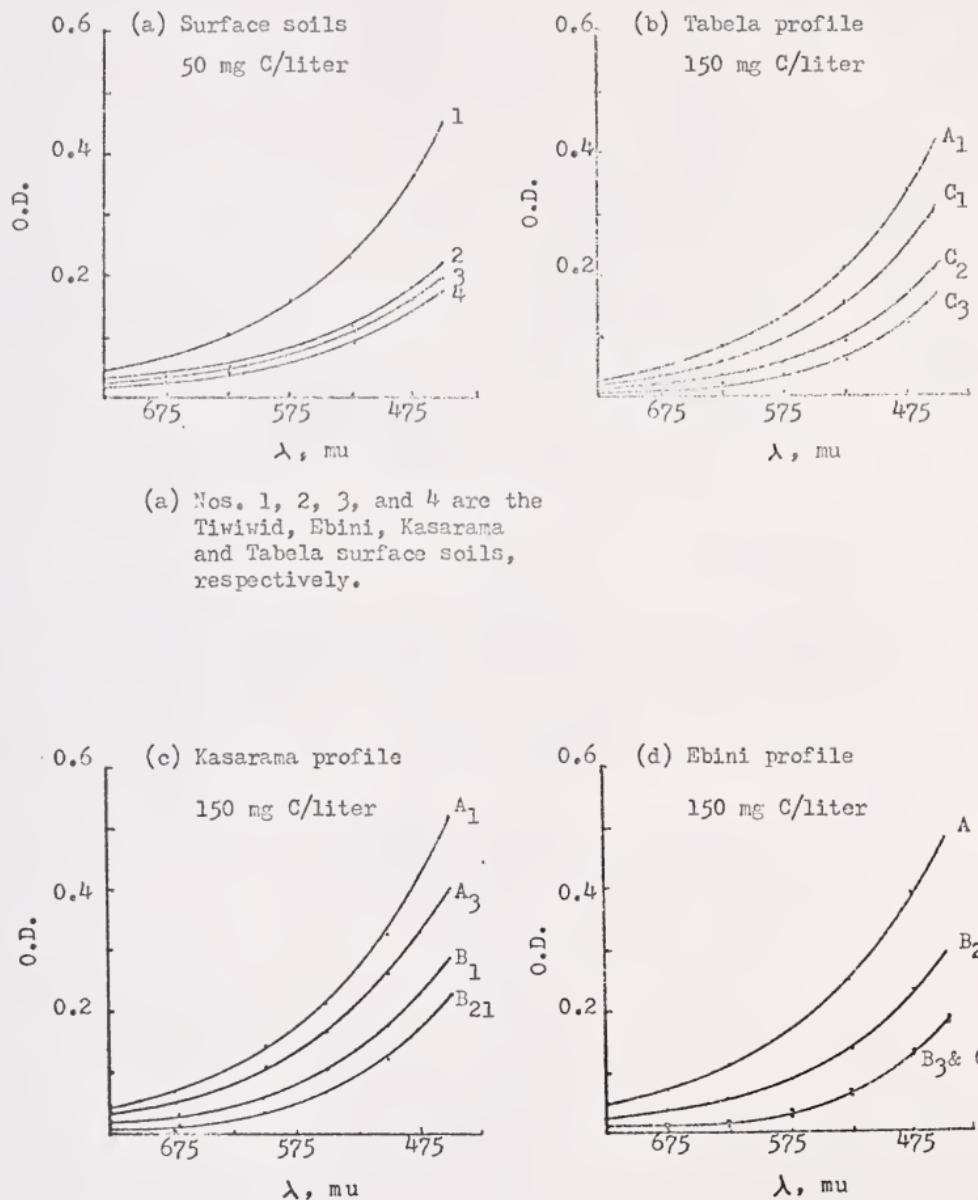


Fig. 5. --Absorption spectra of 0.5 N NaOH extracts.

Table 5. --Percentages of soil organic C extracted by 0.5% NaOH with humic-C/fulvic-C and C/N ratios.

Soil	Horizon and depth cm	Soil C extracted %	C/N	humic-C/ fulvic-C
Tiniwid sand	Surface	35.51	17.80	1.60
Tabela sand	A ₁ 0 - 20	32.11	15.40	0.18
	C ₁ 20 - 50	31.11	16.40	0.00
	C ₂ 50 - 90	33.30	13.00	0.00
	C ₃ 90 - 120	31.50	8.70	0.00
Kasarama loamy sand	A ₁ 0 - 25	37.81	17.70	0.27
	A ₃ 25 - 40	28.00	18.50	0.00
	B ₁ 40 - 55	26.10	11.30	0.00
	B ₂ 55 - 85	27.30	9.70	0.00
Ebinid sandy loam	A 0 - 20	37.78	22.90	0.32
	B ₂ 20 - 75	32.30	17.90	0.00
	B ₃ 75 - 90	30.80	16.30	0.00
	C ₃ 90 - 120	30.60	21.40	0.30

Table 6. --Patterns of precipitation of C in NaOH extracts with variation in pH.

Soil	Horizon and depth cm	C Ext'd. mg/g	pH						
			1	2	3	4	5	6	7
<hr/>									
Tiwivid sand	Surface	6.22	61.75	56.81	--	--	--	--	--
Tabela sand	A ₁ 0 - 20	2.49	14.96	16.46	29.92	52.36	26.93	13.46	11.97
	C ₁ 20 - 50	1.92	--	--	19.36	46.71	37.01	27.26	11.77
	C ₂ 50 - 90	0.93	--	--	--	55.58	47.65	31.75	12.01
	C ₃ 90 -120	0.63	--	--	--	52.56	40.89	29.18	11.67
Kasarama loamy sand	A ₁ 0 - 25	3.39	21.00	22.10	40.89	58.58	48.63	21.00	16.58
	A ₃ 25 - 40	2.01	--	11.18	22.33	42.80	35.35	31.64	11.17
	B ₁ 40 - 55	0.90	--	--	4.15	49.64	45.49	33.08	12.41
	B ₂ ₁ 55 - 85	0.75	--	--	--	49.64	39.69	9.91	--
Ebini sandy loam	A 0 - 30	4.44	23.98	24.84	46.84	62.53	46.25	33.40	18.84
	B ₂ 30 - 75	1.50	--	--	9.93	44.67	32.25	19.85	7.44
	B ₃ 75 - 90	0.81	--	--	--	32.58	27.92	18.62	4.66
	C 90 -120	0.75	--	--	--	24.80	24.80	9.91	--

from the brown sand soils was redissolved at approximately pH 10 in the case of the surface horizons, and at about pH 7.5 to 9.0 in the subsurface horizons. The pH of maximum precipitation of C is not far different from the pH 4.8 level postulated by Waksman (317) as the point of precipitation of β -humus. This material is known to be of high ash content, and has been described as being largely Al with some organic material (317), or as consisting of organic matter entrapped by mineral matter during fractionation (286).

The amounts of Al in the alkali extracts and in the supernatant solutions at the different pH levels are shown in Table 7. It is clear that the minimum amounts of Al remained in solution at about pH 5. In the brown sand soils, the parallel solubilities of alkali extracted C and Al in relation to pH changes bear some similarity to the solubility patterns of C and Al in alkali extracts from the spodic horizons of some Florida soils (341). The insolubility of C and Al in the latter case was considered to have been due to either the occurrence of a direct chemical reaction, or to the co-precipitation of forms of the two elements. Since this pattern was observed in the extracts from spodic horizons (341), and the organic matter in such horizons has been shown to be largely fulvic in character (336), it would seem that the phenomenon involved fulvic rather than humic-C. Fulvic acids are known to react with Al (10, 271), and this suggests that the occurrence of a direct chemical reaction is the more likely mechanism. Positively charged monomeric hydroxy-Al ions have a pK value of about 5 (138), and the functional groups of fulvic acids must, because of their similarity to those of humic acids, have pK

Table 7. --The concentration of Al in the supernatant of the 0.5N NaOH extract at various pH levels.

Soil	Horizon and depth	NaOH Ext'd. Al	Al in supernatant pH					
			1	2	3	4	5	6
Tiwiwid sand	Surface	106	--	--	--	--	--	--
Tabelia sand	A ₁ 0 - 20	725	713	663	538	50	113	225
	C ₁ 20 - 50	912	875	800	88	50	88	195
	C ₂ 50 - 90	1238	--	750	75	23	45	188
	C ₃ 90 - 120	1250	--	550	63	23	23	170
Kasarama loamy sand	A ₁ 0 - 25	1238	1088	1075	925	88	113	313
	A ₃ 25 - 40	1400	1150	1063	50	30	56	200
	B ₁ 40 - 55	1725	--	1475	--*	23	23	213
	B ₂ 55 - 85	1875	--	1638	88	8	45	200
Ebinu sandy loam	A 0 - 20	1238	1088	992	663	105	213	200
	B ₂ 20 - 75	1463	1250	1238	88	8	30	163
	B ₃ 75 - 90	1468	--	1250	45	30	30	150
	C 90 - 120	1375	--	1150	30	8	--*	125

* Sample silt.

values in the range 4.1 to 6.2 (182, 235). Adsorption reactions are likely to be preceded by chelation of Al by "salicylate structures" (271), and then by the formation of nuclei from which a dispersed precipitate can develop (43). The neutralization of charge by adsorption may result in flocculation. The capacity of Al to cause flocculation of organic matter (183) and the effect of the valence of the ionic form on its efficiency in this context (175) support the possibility of the occurrence of direct chemical reaction. Further support is derived from the close agreement of computations based on laboratory preparations and measurements made on soil samples showing that Al-fulvate complexes involved $\text{Al}(\text{OH})^{2+}$ and had maximum stability when all the functional groups of fulvic acid were neutralized (271).

Relatively large amounts of organic C (38 to 75%) were not precipitated at pH 5, even though at this pH the extracts were almost completely decolorized. Possibly the non-precipitated C was in the form of polysaccharides (291) and/or simple organic acids (286).

The behavior of Fe in the alkaline extracts from the surface horizons of the three brown sand soils is similar to that of Al in that there is again a pH of minimum Fe solubility. The data in Table 8 show that minimum solubility of extracted Fe occurred at pH 5 in the Kasarama and Ebini soils, but at pH 6 in the Tabela soil. The solubility pattern was possibly also related to the formation of Fe-organic matter complexes, but the mechanisms involved were much less obvious than those involving Al. The higher pH for

Table 8. --Concentration of Fe in the supernatant of the 0.5N NaOH extract of surface horizons at various pH levels.

pH	Soil		
	Tabela sand	Kasarama loamy sand	Ebini sandy loam
	Fe, ppm		
1	72	10	11
3	56	7	10
4	40	5	5
5	32	3	4
6	13	6	13
7	21	16	20

maximum precipitation in the Tabela soil was perhaps due to the approximately 1:1 ratio of Fe:Al in the alkaline extract as compared to corresponding ratios of 1:2 in the extracts from the Kasarama and Ebini soils (Table 9). The more stable Fe-humates (299) are, therefore, likely to be of greater importance in the Tabela soil, in light of the preferential bonding of Fe by humic acids (290, 292). However, though Fe-fulvates break down at pH > 4.0, this breakdown is only partial (83, 299), thus distinction of the roles or relative importance of the fulvate and humate complexes of Fe is impractical. In the alkali extracts from the profiles, the decreasing amounts of Fe and increasing amounts of Al emphasized the increasing importance of fulvic acids with depth in the profile. Similar trends noted in Indonesian soils were interpreted in terms of preferential bonding of Al by fulvic acids and of Fe by humic acids (290, 292). The progressively higher Al concentrations also suggested the stabilization of fulvic acid down the profile. The amounts of Ca, Mg, K, and Mn removed by the alkali are also indicated in Table 9. The amounts of Ca and Mg were remarkably constant with depth in the profile, while K increased with depth except in the Tabela soil. These three cations could be associated primarily with the organic material or with the amorphous oxides. Amorphous materials in soils have been shown to be involved in the retention of K (222, 304), but NaOH exerts a solubilizing effect (167), and provides a replacing cation-- Na^+ --so that the true source of the cations must be considered obscure.

Table 9. --Concentration of various cations in 0.5M NaOH extracts of soils.

Soil	Horizon and depth cm	Cations in NaOH extract					
		Al	Fe	Ca, ppm	Mg	Mn	K
Tiwiwid sand	Surface	106	535	405	158	13	344
Tabela sand	A 0 - 20	725	712	400	148	13	120
	C ₁ 20 - 50	912	150	375	153	15	450
	C ₂ 50 - 90	1238	55	363	152	8	312
	C ₃ 90 - 120	1250	75	400	158	0	663
Kasararama loamy sand	A ₁ 0 - 25	1238	620	363	152	8	513
	A ₃ 25 - 40	1400	150	363	153	0	450
	B ₁ 40 - 55	1725	75	375	153	0	538
	B ₂ 55 - 85	1875	65	388	145	0	400
Ebinu sandy loam	A 0 - 30	1238	665	400	153	15	269
	B ₂ 30 - 75	1463	97	385	150	0	588
	B ₃ 75 - 90	1488	55	385	155	8	390
	C 90 - 120	1375	34	385	158	15	625

Chemical Characteristics of the Soils

The total amounts of some elements in the soils are shown in Table 10. The amounts of Al and Fe increased with depth in the profile and this can be readily appreciated in relation to the increasing clay content of the lower horizons. The increase in Fe content is also appreciated in terms of the progressively stronger red-yellow coloration of the lower horizons. The Al content of the C₁ and C₂ horizons of the Tabela soil varied somewhat from the general trend, probably because of the more strongly podzolic nature of this soil. The amounts of Ca were not very different from soil to soil or among horizons of a profile. The amounts seemed to be higher than would be expected from soils which had been subject to such prolonged weathering, and which were virtually free of minerals other than quartz and kaolinite. The amounts of Mg were much less than those of Ca, but much more than those of K. Both Mg and K were present in almost constant amounts, with virtually no variation among soils or horizons. The P contents of the soils were low as indicated, and as expected from the degree of weathering to which the soil materials had been subjected. The amounts of N in the surface horizons of the brown sand soils were strikingly similar, in contrast to the obvious differences in organic matter content. The decrease in N content with increasing depth of the horizon followed the pattern of distribution of organic matter.

The pattern of distribution of organic matter is also followed by the CEC, the individual, and the total amounts of exchangeable cations (Table 11). Both groups of cations also decreased with depth

Table 10. --Total contents of various elements in the soils.

Soil	Horizon and depth cm	Elements in soils									
		Al	Fe	Ce	Mg	K	N	P	Mn	Zn	Ca
Tiwiwid sand	Surface	0.28	0.05	1.20	0.59	0.19	0.17	204	15	14	11
Tabella sand	A ₁ 0 - 20	5.65	1.12	0.57	0.16	0.10	0.12	80	22	18	
	C ₁ 20 - 50	5.28	1.23	0.58	0.18	0.05	0.05	50	25	33	23
	C ₂ 50 - 90	6.40	1.95	1.20	0.59	0.19	0.04	43	80	31	20
	C ₃ 90 - 120	5.85	2.35	1.28	0.59	0.16	0.04	24	100	25	20
Kasarama loamy sand	A ₁ 0 - 25	6.10	0.85	1.28	0.57	0.16	0.09	28	36	35	
	A ₃ 25 - 40	7.15	1.03	1.27	0.59	0.22	0.05	55	100	38	18
	B ₁ 40 - 55	7.30	1.33	1.45	0.62	0.27	0.04	22	130	43	16
	B ₂ 55 - 85	10.25	1.75	1.42	0.62	0.26	0.01	36	110	52	22
	A 0 - 30	12.75	1.03	1.20	0.61	0.24	0.09	30	150	25	20
	B 30 - 75	12.20	1.40	1.28	0.59	0.21	0.02	29	110	39	17
Ebini sandy loam	B 75 - 90	15.80	1.55	1.45	0.61	0.24	0.04	26	130	33	18
	C 90 - 120	16.50	1.67	1.20	0.61	0.23	0.01	14	80	28	14

Table 11. --Cation exchange capacity and exchangeable cations in the soils.

Soil	Horizon and depth cm	CEC NH ₄ OAc pH 7.0	Exchangeable cations meq/100g soil				Total K
			A1	Ca	Mg	NH ₄	
Tiwiwid sand	Surface	4.58	0.47	0.64	0.32	0.28	1.71
Tabela sand	A ₁ 0 - 20	1.80	0.26	0.12	0.10	0.04	0.52
	C ₁ 20 - 50	1.43	0.12	0.11	0.09	0.04	0.36
	C ₂ 50 - 90	1.23	0.03	0.10	0.08	0.03	0.24
	C ₃ 90 - 120	1.00	0.03	0.09	0.08	0.02	0.22
Kasarama loamy sand	A ₁ 0 - 25	2.50	0.40	0.16	0.11	0.05	0.72
	A ₃ 25 - 40	1.85	0.08	0.11	0.09	0.03	0.31
	B ₁ 40 - 55	1.29	0.03	0.06	0.03	0.03	0.22
	B ₂₁ 55 - 85	1.39	0.09	0.10	0.08	0.02	0.29
	B ₂ 85 - 120	1.00	0.10	0.12	0.10	0.02	0.34
	B ₃ 120 - 150	0.50	0.14	0.11	0.05	0.00	0.30
Ebdini sandy loam	A 0 - 20	3.04	0.50	0.25	0.09	0.08	0.65
	B ₂ 30 - 75	1.83	0.25	0.12	0.09	0.03	0.56
	B ₃ 75 - 90	2.04	0.21	0.12	0.09	0.04	0.45
	C 90 - 120	2.50	0.10	0.12	0.10	0.02	0.34

down the profile, and the total amounts of exchangeable cations decreased in the same direction as the organic matter content of the surface horizons. Comparison of the CEC and the total amounts of exchangeable cations in a given horizon indicated that the adsorptive complexes of the different soils were far from saturated. Because of the obvious unsaturation and the appreciable amounts of exchangeable Al, some acidity is to be expected in these soils.

The variations in pH within the profiles of the individual soils are shown in Table 12. In the Tabela profile $\text{pH}_{\text{H}_2\text{O}}$ and $\text{pH}_{\text{N KCl}}$ exhibited the same trends and differed from each other by an almost constant value, except for the C_3 horizon. In the Kasarawa profile, the $\text{pH}_{\text{H}_2\text{O}}$ of the A_1 horizon was rather high, and this differed widely from the $\text{pH}_{\text{N KCl}}$ value. The remaining horizons of this soil displayed the same parallel relationship between $\text{pH}_{\text{H}_2\text{O}}$ and $\text{pH}_{\text{N KCl}}$ with differences of the same magnitude as in the Tabela profile. The A and C horizons of the Ebini soil had relatively high $\text{pH}_{\text{H}_2\text{O}}$ values which also differed widely from the $\text{pH}_{\text{N KCl}}$ values. The B horizons of this soil were comparable to the upper three horizons of the Tabela soil in their $\text{pH}_{\text{H}_2\text{O}}$ and $\text{pH}_{\text{N KCl}}$ relationships.

The difference between $\text{pH}_{\text{H}_2\text{O}}$ and $\text{pH}_{\text{N KCl}}$ has been attributed to the effects of the hydrolysis of Al liberated by N KCl (283) and this would appear to provide a part of the explanation in this case. The amounts of N KCl exchangeable Al (Table 13) decreased down the profile as $\text{pH}_{\text{N KCl}}$ increased, but the virtually constant differences between $\text{pH}_{\text{H}_2\text{O}}$ and $\text{pH}_{\text{N KCl}}$ suggested that the explanation is not complete.

Table 12. --pH values in the different horizons of the soils and the relationship between values by different methods of measurement.

Soil	Horizon and depth	pH		N KCl:soil 10:1 (b)	Difference (a)-(b)
		H ₂ O:soil 1:1 (a)	N KCl:soil 10:1 (b)		
Tiwiwid sand	Surface	4.20	3.95		0.35
Tabela sand	A ₁ 0 - 20	5.40	4.80	0.60	
	C ₁ 20 - 50	5.60	4.95	0.65	
	C ₂ 50 - 90	5.65	5.00	0.65	
	C ₃ 90 - 120	5.55	5.25	0.25	
Kasarama loamy sand	A ₁ 0 - 25	5.70	4.65	1.05	
	A ₂ 25 - 40	5.35	4.70	0.65	
	B ₁ 40 - 55	5.60	5.00	0.60	
	B ₂ 55 - 85	5.50	4.35	0.65	
Ebinli sandy loam	A 0 - 30	5.50	4.50	1.00	
	B ₂ 30 - 75	5.40	4.80	0.60	
	B ₃ 75 - 90	5.40	4.20	0.50	
	C ₃ 90 - 120	5.80	4.80	1.00	

Table 13. --Amounts of Al extracted from soils by different reagents at different pH levels.

Soil	Horizon and depth cm	Extractant					
		0.5N NaOH pH 12.2	CBD pH 8.5	N KCl pH 5.7	N NH ₄ OAc pH 4.8	0.1N HCl pH 1.10	Al extracted, ppm
Tiwiwid sand	Surface	106	61	42	10	20	
Tabela sand	A ₁ 0 - 20	725	875	24	70	100	
	C ₁ 20 - 50	912	1313	11	70	130	
	C ₂ 50 - 90	1238	1812	3	75	185	
	C ₃ 90 - 120	1250	1250	5	70	180	
Kasarama loamy sand	A ₁ 0 - 25	1238	1063	36	100	195	
	A ₂ 25 - 40	1400	875	7	95	230	
	B ₁ 40 - 55	1725	1125	3	70	280	
	B ₂ 55 - 85	1875	1063	8	80	280	
	A 0 - 30	1238	938	45	95	230	
	B ₂ 30 - 75	1463	1325	23	120	270	
Ebinu sandy loam	B ₃ 75 - 90	1488	1625	19	110	275	
	C 90 - 120	1375	1738	9	125	285	

The inadequacy of the hydrolysis effect as the explanation for the difference in pH values with different methods of measurement was reiterated by the low pH levels of the Tiwiwid soil and the small difference of the two values, relative to the amount of M KCl exchangeable Al present in this soil. In the brown sand soils, the $\text{pH}_{\text{N}} \text{KCl}$ values all were within the range 4.70 to 5.35 M KCl which is known to be the range of neutralization of exchangeable Al (16, 340).

The possible importance of Al in these soils was examined by comparison of the amounts of Al removed by different extracting solutions. It can be seen from Table 13 that the highest amounts were removed by 0.5 M NaOH and citrate-bicarbonate-dithionite (CBD). The CBD extracted Al was more than the NaOH extracted Al in the upper three and lower two horizons of the Tabela and Ebini soils, respectively, while alkali extracted Al exceeded CBD extracted Al in all horizons of the Kasarama soil, in the upper two horizons of the Ebini soil, and in the Tiwiwid sample. Larger amounts of Al were extracted from the latter soil by M KCl than by either M NH_4OAc (pH 4.8) or 0.1 M HCl. In every other case, M KCl removed the smallest amount of Al, relative to the three acid extractants. In the profiles M KCl extracted Al decreased as the depth of the horizon increased, while Al removed by M NH_4OAc (pH 4.8) showed a generally increasing trend. All other extractants removed more Al from lower horizons.

Alkaline extractants tend to remove hydroxy-Al (345). The Al removed by the CBD extractant is associated with amorphous materials (161, 319, 342) but should also include Al from organic complexes

since the organic material was destroyed by H_2O_2 oxidation prior to Al extraction. The alkali extracts Al as organic complexes (159, 167), and would be expected to remove less Al than CBD. Possibly, the higher pH of the alkali extractant and its destructive effects on the H-bonds and polymer size of the organic substances (181) may have facilitated a more complete removal of Al complexed by organic matter as well as the dissolution of Al from kaolinite in the more advanced stages of crystalline degradation. Two of the acid extractants are also known to remove Al complexed organic matter. Dilute acids extract fulvate complexes of mobile forms of hydroxy-Al (159) while NH_4OAc (pH 4.8) removes some organic matter-Al complexes (230, 345). This latter category of extracted Al, though not very well defined, is regarded as comprising exchangeable and other soluble forms of Al (232), and has been described as acidic-Al (230). The Al removed by KCl is exchangeable and bears either a curvilinear (51, 234) or linear (135) inverse relationship to the pH of the soil. This form of Al has been implicated in equilibrium conditions in the soil, with non-exchangeable acidic-Al (230) and with 'net' CEC (248). On the basis of the wide differences between the amounts of exchangeable Al and those extracted by other reagents, it would seem that the brown soils are Al-buffered systems (138). In the Tiwiwid soil, the major portion of the extractable Al was exchangeable, and this suggests that the extent of Al-buffering in this soil is extremely limited.

Surface SoilsBuffering Capacity

The titration curves shown in Fig. 6, point to the importance of the organic fraction in the buffering of the soils. The greatest degree of buffering occurred in the Tiwiwid, and the least in the Tabela soil, while the Kasarama was only slightly less buffered than the Ebini soil. The direction of increase in buffering capacity was the same as that of increase in humic and of decrease in fulvic-C. The trends were most likely due to differences in the acid strength of the organic matter in the different soils (169), since the clays were all of the same type, and only poorly crystalline. The acid strength of fulvic acid is greater than that of humic acid (336), and, therefore, soils higher in fulvic acid content would be expected to have lower buffering capacities.

Cation Exchange Capacity

Buffering capacity is directly related to CEC, and, therefore, to the materials which provide the exchange sites. Using the CEC data for the upper two horizons (Table 11), simultaneous equations of the form $Y = aX_1 + bX_2$, where X_1 and X_2 are the clay and organic matter contents respectively, in the soil, Y is the measured CEC, and a and b are constants, showed that the organic matter supplied more than 90% of the CEC in each of the brown sand soils (Table 14). The CEC of the organic matter varied from 197.5 meq/100g soil in the Tabela to 160.7 meq/100g in the Kasarama, while the clay fraction had

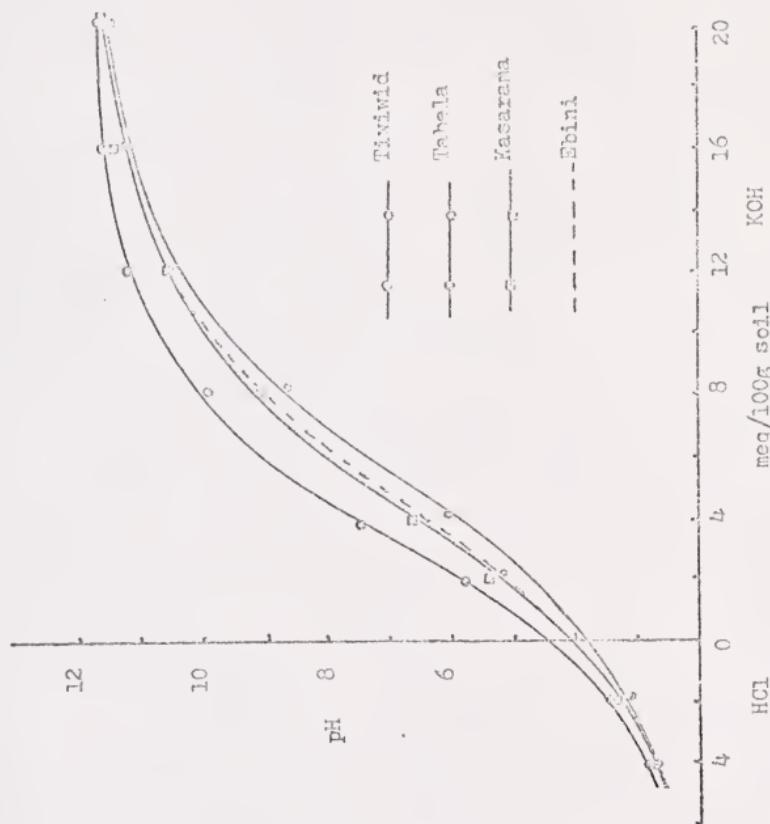


Fig. 6. --Titration curves of surface horizons in N-KCl modified with HCl or KOH .

Table 14. --Contributions to soil cation exchange capacity by the clay and organic matter fractions.

Soil	CEC		CEC due to OM %
	OM	Clay meq/100g	
Tabela sand	197.5	3.72	100
Kasarama loamy sand	160.7	1.53	91.7
Ebini sandy loam	164.5	0.68	96.7

a maximum of 1.53 meq/100g in the Kasarama, and a minimum value of -3.72 meq/100g in the Tabela. The negative quantity, no doubt, indicated that the positive charge on amorphous hydroxy Al and Fe exceeded the negative charge in the crystalline clay.

Multiple regression analysis of the CEC for the four surface horizons yielded the equation:

$$Y = 0.029 + 0.004X_1 + 1.650X_2; r^2 \text{ (for } X_1 \text{ and } X_2) = 0.99$$

where Y represents the CEC, and X_1 and X_2 are the clay and organic matter percentages, respectively. An average value for the CEC of the organic fraction of the soil was thus 165 meq/100g, while a comparable value for the clay fraction was 0.40 meq/100g.

Measurements of CEC in soils which contain appreciable amounts of sesquioxides have shown that the sesquioxides exert considerable influence on the measured CEC (29, 66). The saturating cation used in the determination also influences the CEC values obtained (76), and as shown in Table 15, the CEC of the soils varied considerably. It is surprising that the CEC values obtained by the N KCl method were the highest, rather than the lowest. The high values were undoubtedly related to the larger amounts of Al released from the soil by KCl saturation and the use of Ca^{2+} as the replacing cation. The only reason which can be advanced for the removal of different amounts of Al from the same soils by the same reagent is that approximately 2 years elapsed between measurements, but this does not justify increases of -0.14, 0.38, 0.70, and 0.67 meq Al/100g soil in the Tiwiwid, Tabela, Kasarama, and Ebini soils, respectively,

Table 15. --Cation exchange capacity measurements.

Soil	CEC				
	N KCl pH 5.7	N NH ₄ OAc pH 7.0	BaCl ₂ pH 7.0	H ₂ SO ₄ pH 1.0	NaOAc pH 7.0
Tinigid sand	5.59	4.58	4.40	4.34	5.61
Tabelia sand	2.47	1.90	2.07	0.26	2.33
Kasarama loamy sand	4.29	2.50	3.24	0.32	3.66
Ebini sandy loam	5.20	3.04	3.95	0.30	4.25

in the later measurement of exchangeable Al. The established sequence of measured CEC Σ KCl < Σ NH₄OAc (pH 7.0) < BaCl₂-TEA (pH 8.2) (66) incorporates a pH effect, but it has been shown that an additional source of variation still remains (76). It seemed that the differences in the composition of the organic fractions of the soils might account for some of this unexplained variation. Since the fulvate salts of the saturating ions are all soluble and, therefore, likely to be removed in the initial process of leaching, simple regression analyses were run on the Σ KCl and Σ NH₄OAc estimates of CEC. The curves in Fig. 7 indicate that the measured CEC was related to the humic acids.

When all soils were considered, the humic-C had average values of 215 and 186 meq/100g, by the NH₄OAc and KCl methods, respectively. These values are comparable to those computed for the organic fraction as a whole, and suggest that the possible removal of fulvic acids by monovalent saturating cations warrants some consideration. The distribution of the points indicates that the brown sands may, in fact, belong to a different population from the Tiwiwid sand. Indeed the regression equations for all the soils were:

$$Y_1 = 1.90 + 2.15X; r = 0.96$$

$$Y_2 = 3.45 + 1.86X; r = 0.71$$

as compared to those for the brown sands only:

$$Y_1 = 1.16 + 5.38X; r = 0.99$$

$$Y_2 = 1.15 + 11.83X; r = 0.98$$

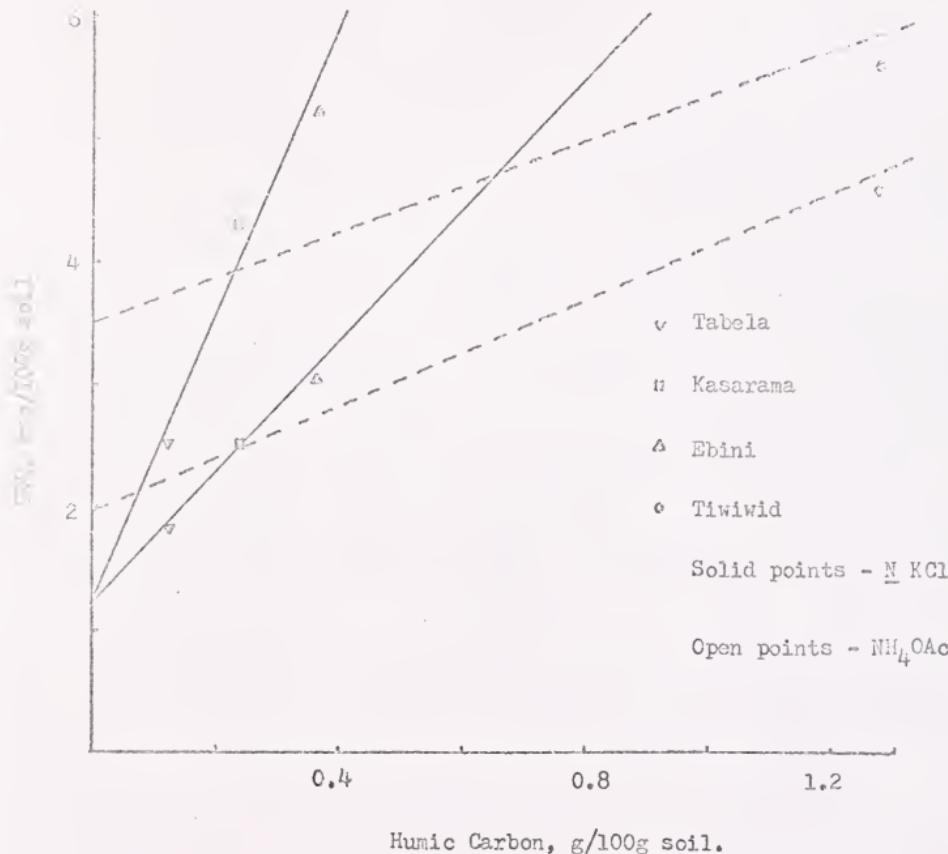


Fig. 7. --Cation exchange capacity in relation to humic-carbon.

where Y_1 and Y_2 represent the CEC measurements by NH_4OAc and KCl, respectively, and X represents humic-C. The larger values for CEC of humic-C in the latter equations are comparable to the total CEC of 680 meq/100g reported by Wagner and Stevenson (316) for humic acids and 1,100 meq/100g reported by McKeague *et al.* (188) for extracts from a spodic horizon. The higher values in the H KCl equation probably resulted from the larger amounts of Al removed from the soils.

Incubation Studies

The soils were incubated in order to ensure complete neutralization of added lime and to permit the measurement of the resulting changes in pH. It was found that pH changes varied from the predictions based on the titration curves (Fig. 6) by ± 0.3 pH units. Incubation was effected at field capacity by the addition of 5.3, 6.0, 8.0, and 9.5% (w/w) of distilled water to the Tiwiwid, Tabela, Kasarama, and Ebini soils, respectively.

Cation retention

The effects of pH and added P on the retention of cations added to the limed soils followed the same general patterns. Liming enhanced the leaching of K and Mg from each soil. Substantial amounts of Ca were also in leachable forms (Table 16). The Tiwiwid sand retained < 27% of the Ca added in leachable forms while as much as 95, 52, and 34% were leachable in the Tabela, Kasarama, and Ebini soils, respectively. The trend was similar to that of the fulvic acid contents, and suggested that

Table 16. --Ratio Ca leached:exchangeable Ca at different pH levels and rates of P application.

Soil	(N KCl) pH range	P applied, ppm			150
		0	50	100	
Tiwiwid sand	3.80-3.85	0.01	0.13	0.11	0.11
	4.95-5.50	0.13	0.10	0.10	0.10
	5.60-6.25	0.19	0.12	0.15	0.17
	6.50-7.15	0.26	0.17	0.17	0.19
Tabella sand	5.05-5.20	0.88	0.86	0.55	0.40
	5.95-6.10	0.67	0.53	0.52	0.32
	6.60-6.70	0.95	0.55	0.58	0.34
	7.80-8.20	0.76	0.57	0.42	0.33
Kasararama loamy sand	4.90-5.00	0.21	0.17	0.03	0.11
	5.90-6.00	0.42	0.08	0.17	0.18
	6.20-6.70	0.52	0.40	0.23	0.28
	7.10-7.80	0.52	0.29	0.32	0.30
Ebini sandy loam	4.50-4.60	0.15	0.24	0.20	0.11
	5.45-5.70	0.26	0.19	0.12	0.08
	6.20-6.50	0.27	0.20	0.17	0.12
	6.80-6.95	0.34	0.26	0.19	0.27

leachable Ca was present as fulvate salts. Exchangeable Ca increased with increase in pH, and was probably in the form of Ca-humates. The addition of 50 ppm P to the Tiwiwid sand decreased the amount of Ca in leachable form except in the case where no lime was added. Further additions of P caused no change in the relative amounts of leachable Ca. The depressing effect of P on the amounts of leachable Ca occurred in each of the brown sand soils at 150 ppm level of P additions. This effect was apparently not due to the formation of Ca-P compounds (49, 55, 86) since the insolubility of such compounds would be expected to cause the amounts of exchangeable Ca to remain constant or to decline. The proportions of Ca in leachable form would, therefore, also be expected to remain constant or to increase. The apparent disappearance of the 'P-effect', as the 50ppm level was exceeded in the Tiwiwid sand, supports the possibility that Ca-P compounds were not formed. The persistence of the 'P-effect' in the brown sand soils suggested that added P made a definite contribution to the negative charges of these soils.

The total amounts of exchangeable cations held against leaching followed the same pattern seen for Ca. The data for the Tiwiwid sand are presented in Table 17. However, the individual cations differed in patterns of retention. The amounts of Mg retained increased initially and then declined. The increase appeared to be consequent upon the addition of 50ppm P. Amounts of K retained showed an increasing trend with addition of P, perhaps because KH_2PO_4 was the source of P used. Like Mg, the amounts of K retained decreased with

Table 17. -Pattern of retention of exchangeable cations against leaching as affected by pH and rate of P application on Pumid sand.

pH range	Exchange-cation	P applied rpm		
		50	100	150
3.80-3.85	Ca	0.99	0.99	0.99
	Mg	0.42	0.63	0.60
	K	0.01	0.12	0.20
	Total	1.42	1.74	1.77
4.95-5.50	Ca	2.73	2.77	2.65
	Mg	0.43	0.49	0.41
	K	0.00	0.10	0.01
	Total	2.16	3.36	3.07
5.60-6.25	Ca	3.66	3.99	4.05
	Mg	0.39	0.60	0.42
	K	0.00	0.02	0.12
	Total	4.05	4.61	4.65
6.50-7.10	Ca	5.13	5.65	5.15
	Mg	0.28	0.45	0.41
	K	0.00	0.05	0.11
	Total	5.41	6.15	5.67

increase in pH; thus, the total amount of exchangeable cations retained was mainly Ca, and the proportion of Ca in each total increased with increase in pH. Tables 18, 19, and 20 show comparable data for the Tabela, Kasarama, and Ebini soils, respectively. In each case trends were similar to those seen in the Tiwiwid sand, except for the increase in exchangeable Ca which occurred with each increment of added P provided some lime had also been added. The total amounts of exchangeable cations retained by each of the soils increased with increase in pH. This is readily appreciated as a consequence of increased CEC due to the increased pH-dependent CEC (120) and the freeing of exchange sites previously blocked by Al (29) and/or Fe (65).

Phosphate retention

The P added to the soils was found to vary in its degree of solubility in water, as shown in Table 21. In the Tiwiwid sand, 38 to 60% of the added P remained water soluble, regardless of the level of P addition. In the absence of added P, and at the 50ppm level, increasing the pH depressed the amount of P in the water soluble form. This depressing trend was not obvious at the 100 and 150ppm P levels. In the Tabela sand < 11% of the added P remained water soluble, the proportions increasing from 2.3 to 6.6% at the 50ppm level, to 3 to 12% at the 150ppm level. Increased pH seemed to increase the amount of water soluble P in this soil. The proportions of water-soluble P in the Kasarama soil were similar to those in the Tabela soil, while those in the Ebini soil were much lower, and seemed to decrease with increasing pH.

Table 18. --Pattern of retention of exchangeable cations against leaching as affected by pH and rate of P application on Tabela sand.

pH range	Exch. cation	P applied, ppm		
		0	50	100
<u>150</u>				
5.05-5.20	Ca	0.20	0.16	0.25
	Mg	0.07	0.18	0.17
	K	0.00	0.00	0.19
	Total	0.27	0.34	0.61
5.95-6.10	Ca	0.61	0.64	0.65
	Mg	0.03	0.15	0.15
	K	0.00	0.01	0.05
	Total	0.64	0.80	0.86
6.60-6.70	Ca	1.21	2.37	1.49
	Mg	0.10	0.13	0.13
	K	0.00	0.01	0.05
	Total	1.31	1.51	1.67
7.80-8.20	Ca	2.35	2.65	2.99
	Mg	0.20	0.18	0.17
	K	0.00	0.00	0.00
	Total	2.55	2.83	3.16

Table 19. --Pattern of retention of exchangeable cations against leaching as affected by pH and rate of P application on Kasararama loamy sand.

pH range	Exch. cation	P applied, ppm		
		0	50 -Mg/100g-	100 -Mg/100g-
4.90-5.00	Ca	0.26	0.36	1.11
	Mg	0.23	0.25	0.17
	K	0.05	0.00	0.00
	Total	0.64	0.61	1.28
5.90-6.00	Ca	1.20	1.26	1.37
	Mg	0.18	0.21	0.26
	K	0.00	0.00	0.00
	Total	1.38	1.47	1.63
6.20-6.70	Ca	2.06	2.25	2.02
	Mg	0.22	0.20	0.18
	K	0.00	0.00	0.07
	Total	2.28	2.45	2.27
7.10-7.80	Ca	3.57	3.56	3.42
	Mg	0.24	0.25	0.26
	K	0.00	0.00	0.00
	Total	3.81	3.81	3.68
3.63				

Table 20. --Pattern of retention of exchangeable cations against leaching as affected by pH and rate of P application on Ebin sandy loam.

pH range	Exch. cation	P applied, ppm		
		0	50 req./100g	100
4.50-4.60	Ca	0.41	0.37	0.44
	Mg	0.54	0.54	0.51
	K	0.03	0.06	0.13
	Total	0.98	0.97	1.08
5.45-5.70	Ca	1.42	1.52	1.49
	Mg	0.42	0.52	0.47
	K	0.03	0.11	0.11
	Total	1.87	2.15	2.07
6.20-6.50	Ca	2.45	2.52	3.16
	Mg	0.41	0.44	0.47
	K	0.00	0.00	0.04
	Total	2.86	2.96	3.67
6.80-6.95	Ca	3.86	3.88	3.93
	Mg	0.40	0.41	0.36
	K	0.04	0.03	0.01
	Total	4.30	4.32	4.20

Table 21. —Water soluble phosphorus in surface soils incubated at different pH levels and rates of applied P.

Soil	pH N KCl range	P applied, ppm			H ₂ O-soluble P, ppm
		0	50	100	

Tiwiwid sand	3.80-3.85	6.45	25.50	63.75	73.90
	4.95-5.50	4.80	28.50	48.75	75.00
	5.60-6.25	3.60	26.25	61.50	96.00
	6.35-7.15	3.15	22.50	55.50	78.00
Tabella sand	5.05-5.20	0.00	1.15	7.35	14.40
	5.95-6.01	0.00	1.88	9.90	7.50
	6.60-6.70	0.00	3.20	6.45	18.30
	7.80-8.20	0.00	2.75	10.20	15.30
Yasarama loamy sano.	4.90-5.00	0.00	1.80	10.80	14.40
	5.90-6.00	0.00	1.43	8.40	12.60
	6.20-6.70	0.00	1.75	9.45	16.80
	7.10-7.80	0.00	2.20	7.30	10.20
Ebini sandy loam	4.50-4.60	0.00	0.30	4.65	7.50
	5.45-5.70	0.00	0.00	4.38	9.90
	6.20-6.50	0.00	0.00	5.25	8.90
	6.80-6.95	0.00	0.00	3.00	6.15

Table 22 shows the amounts of P removed by the Bray #1 extractant. In the Tiwiwid soil, virtually all the P added was removed at the 50ppm level, while 85 to 100% was removed at the 100ppm level, and 72 to 90% at the highest level of P addition. The proportions removed from each of the brown sand soils were similar: 32 to 56% at the 50ppm, 37 to 68% at the 100ppm, and 37 to 50% at the 150ppm P levels, respectively. The trends of P extractability by the Bray #1 extractant were not very consistent. Extractable P seemed to increase with pH in the Tabela soil except at the zero P level, but this trend was less obvious at the higher P levels. In the Kasarama soil, there seemed to be a decreasing trend at the 50ppm P level, but an increasing trend at the 100 and 150ppm P levels. In the Ebini soil, extractable P appeared to decrease with increase in pH.

The Bray #1 extractant removed the more readily soluble portions of each form of available soil P, and may thus have extracted P from Ca-P, and Fe-P compounds formed in the soils. The amounts of Ca-P were unlikely to have been appreciable, as indicated by the increasing amounts of exchangeable Ca found at the higher levels of lime. The amounts of P obtained from Al-P compounds were likely to have been of much greater importance than those from Fe-P compounds, because of the relatively larger quantities of Al than Fe in the soils (330), and because fractionation studies (55, 118, 178, 275, 347) have shown that Al-P is frequently the form of soil P which is increased most on the addition of P to the soil. Further,

Table 22. —Bray #1 extractable P in soils incubated at different pH levels and with different rates of applied P.

Soil	pH N KCl Range	P applied, ppm			
		0	50	100	150
Tin wild sand	3.80-3.85	5	50	105	135
	4.95-5.50	5	45	88	117
	5.60-6.25	5	50	90	108
	6.50-7.15	8	63	85	133
Tabela sand	5.05-5.20	2	20	59	66
	5.95-6.10	0	28	61	56
	6.60-6.70	1	28	41	68
	7.80-8.20	0	23	57	73
Kasararama loamy sand	4.90-5.00	1	27	46	63
	5.90-6.00	0	27	63	56
	6.20-6.70	1	19	47	72
	7.10-7.80	1	23	68	68
Ebin1 sandy loam	4.50-4.60	1	22	41	62
	5.45-5.70	1	18	41	59
	6.20-6.50	0	16	40	60
	6.80-6.95	1	23	37	50

the trends of P retention against extraction increased in a direction similar to that of increasing extractable Al content being least in the Tiwiwid sand and highest in the Ebini soil. Several reports attest to the possible reaction of P with extractable Al (244, 293), exchangeable Al (62, 132), Al complexed by organic matter, and Al in gibbsite and kaolinite (176, 177, 249). The absence of gibbsite and the different amounts of Al extracted from the soils by different reagents suggested that Al complexed by organic matter was the most likely source of Al for reaction with P. The possible contribution of Fe-P compounds to the extracted P cannot be ignored, since hydrous Fe oxides (226, 330), and Fe complexed by organic matter (168, 320) are both capable of reacting with P.

Soil Properties in Relation to Potential Soil Fertility

The absence of samples of subsurface horizons of the Tiwiwid sand precluded valid comparisons of the profiles. However, data adduced by Bleackley and Khan (31, 32) indicated that the Tiwiwid sand has been subjected to a considerable degree of podzolization. The three profiles examined displayed some differences, but these were differences in degree only. It would appear from the trends in the contents of organic matter, amorphous materials, and clay, that the three soils are similar in origin and have passed through the same developmental processes. The brown sand soils seemed to differ, as a group, from the Tiwiwid sand, and though all the soils were kaolinitic, the apparent differences were reiterated by comparisons

of the surface horizons of the soils. The differences were seen in the composition of the organic fraction, in the contents of amorphous materials, and in the soil contents and patterns of P retention.

The similarities in the four soils were seen in the patterns of cation retention and in the potential for loss of cations by leaching. These similarities originated in the sizeable contributions to the negative charges of the soils, by the organic fraction. The clay fractions were relatively small in each of the soils and contained poorly crystalline kaolinite, probably as mute testimony of the millenia of weathering to which the soils have been subjected (119, 303). Indeed, the soils conformed taxonomically to the CEC-source groupings found by Yuan *et al.* (346). They also conformed to the predictions of Spencer (284), since with more than 90% of the CEC due to the organic fraction in each case, Ca was apparently preferentially bonded, while K and Mg were virtually excluded. The high potential for loss of K and Mg by leaching, and to a lesser extent, the relatively large amounts of Ca which were held in leachable form, offer some explanation for the failure of added fertilizers to have any effect on the exchangeable nutrient status of these soils (315). Each soil showed the same type of response in cation retention to pH increase, and though this may have been due in part, particularly at higher pH levels, to the sorption of Ca(OH)^+ ions rather than Ca^{2+} (53, 169, 213), the increased contribution of the pH-dependent CEC (29, 120) must have been the major factor.

The importance of pH-dependent CEC was reflected by the amounts

of titratable acidity as compared to the amounts of exchangeable Al in the soils. The data presented in Table 23 indicated that though there were considerable amounts of acidity in each soil, less than 13% of this was attributable to exchangeable Al in any of the soils. Thus, there must be appreciable numbers of exchange sites which became active as pH was increased, either by the release of non-exchangeable Al or by the dissociation of functional groups (169).

The data presented in Table 23 also indicated the existence of some obvious differences in the soils. The Tiwiwid sand displayed very different degrees of Al and base-saturation as compared to the brown sand soils. The Al-saturation computations based on the more recent measurements in the process of KCl-CEC determinations were approximately 6, 26, 26, and 22% in the Tiwiwid, Tabela, Kasarama, and Ebini soils, respectively. The existence of group differences was reiterated by the higher base saturation of the Tiwiwid sand, with its higher CEC, but lower pH. Exchangeable Al was apparently not the major factor in determination of the pH of this soil. The brown sand soils on the other hand contained less exchangeable bases than exchangeable Al but had higher pH levels. The relative amounts of amorphous Al, and of Al extracted by 0.5N NaOH suggested that these soils complied with the Al-equilibrium conditions postulated by Pioncke and Corey (230).

Each soil showed a positive effect of P addition on the amounts of exchangeable Ca retained, but here again there were differences.

Table 23. --Some characteristics of the four surface soils, summarized.

Soil	pH (N KCl)	Exch.			CEC pH 7.0	% Saturation		
		Acidity pH 8.0	Exch. Al	Exch. Bases		Al	Bases	
		--meq/100g soil--						
Tinigid sand	3.95	4.40	0.47	1.24	4.58	10.26	27.09	
Tabella sand	4.80	2.07	0.27	0.26	1.80	15.00	14.44	
Kasarama loamy sand	4.65	3.34	0.40	0.32	2.50	16.00	12.30	
Ebinu sandy loam	4.50	3.95	0.50	0.30	3.04	16.12	9.87	

The P effect was relatively short-lived in the Tiwiwid sand. Similarly, as indicated by the solubility of added P in water, the Tiwiwid sand sorbed much less P than the brown sand soils, at any of the P levels used. This was to be expected from the contents of clay and of hydrous oxides of Al and Fe in the soils. The virtually complete removal of added P by the Bray #1 extractant from the Tiwiwid sand indicated that P sorption in this soil was reversible with pH, probably because the adsorption process was mainly physical (17), and/or because it was effected largely by kaolinite (207). The greater amounts of P sorbed by the brown sand soils and the partial irreversibility of adsorption suggested that chemisorption (17) was of greater importance, as were the amorphous hydrous oxides (207) in this context, in these soils. Forms of the hydrous oxides were not definitely established, but they were very probably associated with the organic fraction of the soils. The likelihood of involvement of Al-organic matter complexes in P sorption was bolstered by the removal of comparable amounts of Al from the brown sand soils by the 0.5N NaOH and citrate-bicarbonate-dithionite extractants, and by the occurrence of maximum precipitation of alkali extracted C and Al at a pH level close to the pK value of organic matter, to the pK_1 of amorphous Al(OH)_2^+ (138) and to the pH of the untreated soils. The high fulvic acid content of these soils, and the known capacity of fulvate complexes of Al (168) and Fe (168, 320) to react with P, provided further support for the possible involvement of Al-organic matter complexes in P sorption.

So also did the parallel patterns of increase in CEC and P sorption on application of P. The adsorption of P has been shown to increase the negative charge on the adsorbing surface (123, 206), and it was apparently this increase which Mehlich (192, 194, 196) referred to as "CEC due to AEC."

Though the Tiwiwid sand had apparently ample levels of P (Table 21), each of the soils was very poorly supplied with native P. Their contents of exchangeable nutrient cations were also very low, despite surprisingly high total amounts in the soils. The fertility of a soil is determined by the level and nature of acidity, the buffering capacity, and the capacity to retain added nutrients in plant-available forms. The data presented indicated that the soils should be expected to differ in potential fertility, with the most marked sources of the differences dependent on the nature of the buffering systems and the patterns of sorption of P.

Plant GrowthLimiting NutrientsPangolagrass

The variations in average dry matter production of pangolagrass, consequent upon the addition of individual major nutrients, and fritted micronutrients--referred to as Tr--are shown in Table 24. The data for the individual harvests are presented in Table 53 and 54. The main effects of each treatment are summarized in Table 25, and described in terms of the average rates of change. In the absence of a response, the slope computed for a given treatment should be approximately zero (201). Negative slopes could indicate either the existence of severe deficiencies, or of toxicities induced by excessive supplies of the corresponding treatment, as postulated by the generalized Steenberg curve (279).

In the Tiwiwid sand, the response to the addition of S was negative while all other responses were positive. The slopes of the response to N and Tr were approximately 0.9 and 0.6, respectively, implying that on this soil, the growth of pangolagrass was limited primarily by the supply of N, and to a lesser extent by the supply of micronutrients. The F-tests (Table 55) showed that only the N response was significant. In the Tabela soil, all responses were positive with those to N and K being significant, and that to P highly significant. The slope of the P response was extremely steep, suggesting that the supply of P to pangolagrass was far from optimal. The data for the Kasarama soil were identical in meaning to those

Table 24. --Average shoot weights (oven-dried) from two harvests of pangolagrass.

<u>Treatment</u>	<u>Soil</u>			
	<u>Tiwiwid</u>	<u>Tabela</u>	<u>Kasarana</u>	<u>Ebini</u>
	<u>g/pot</u>			
Control	4.40	0.25	2.15	2.20
N	6.90	0.75	0.50	2.10
S	5.95	0.65	0.30	1.00
P	6.25	2.60	4.85	3.65
K	5.10	0.25	1.10	0.90
Tr	5.35	0.25	0.35	1.45
NS	2.60	0.60	1.85	2.20
NP	8.00	3.90	4.25	4.35
NK	8.65	0.40	1.00	1.60
NTr	7.95	0.20	0.40	0.45
SP	4.70	3.60	4.05	4.35
SK	6.40	0.70	1.25	0.95
STr	7.30	0.45	0.75	1.95
PK	5.83	0.90	5.15	3.75
PTr	5.90	3.70	5.05	3.60
KTr	6.20	0.35	0.55	1.95
NSP	7.65	3.70	5.25	5.50
NSK	7.85	0.80	3.05	3.45
NSTR	7.35	0.50	0.90	0.85
NPK	12.25	8.75	9.05	8.85
NPTr	8.55	3.85	3.95	1.10
NKTr	10.85	0.25	0.85	0.80
SPK	4.80	3.75	3.80	4.35
SPTr	7.55	4.20	4.10	4.15
SKTr	6.60	0.35	0.30	0.15
FKTr	5.65	3.80	4.50	2.55
NSPK	2.00	8.15	8.30	8.15
NSPTr	9.10	3.30	6.45	5.65
NSKTr	3.20	0.80	1.95	1.50
NPKTr	9.10	9.30	8.20	8.70
SPKTr	6.60	4.45	5.55	3.30
NSPKTr	11.25	8.20	8.10	2.05

Table 25. --Shoot growth* (oven-dried) of pangolagrass in response to fertilizer applications.

Soil	Treatment	Main effect					
		N	S	P	K	Cr	Tr
Tiwiwid sand	+	123.25	100.9	115.18	112.33	118.50	
	-	94.58	116.93	102.65	105.50	99.33	
	Response	28.67	-16.03	12.53	6.83	19.17	
	Slope	0.896	-0.509	0.392	0.213	0.599	
Tabela sand	+	53.45	144.20	76.15	51.2	43.95	
	-	30.25	39.50	7.55	32.5	39.75	
	Response	23.20	4.70	68.6	18.7	4.20	
	Slope	0.725	0.147	2.144	0.584	0.131	
Kasarama loamy sand	+	64.05	55.95	90.60	62.70	51.95	
	-	43.80	51.90	17.25	45.15	55.90	
	Response	20.25	4.05	73.25	17.55	-3.95	
	Slope	0.633	0.127	2.292	0.548	-0.123	
Ebinu sandy loam	+	57.30	49.55	74.05	53.00	40.20	
	-	40.25	48.00	23.50	44.55	57.25	
	Response	17.05	1.55	50.55	8.45	-17.15	
	Slope	0.533	0.048	1.580	0.264	-0.536	

* Mean of two harvests

+ --Indicates the sum of yields from all pots supplied with fertilizer.

- " " " " not supplied with fertilizer.

for the Tabela soil, except for the negative response to micronutrients. In the Ebini soil, only the response to P was significant, and again, the response to micronutrients was negative.

The root weights of pangolagrass (Table 26) were largest in the Tiwiwid sand, and appeared to reflect beneficial interactions of K with the other nutrients supplied. In the brown sand soils, maximum root growth was obtained when N, S, P, and micronutrients were supplied together. Like shoots, root weights in the control treatments increased in the order: Tabela < Ebini < Tiwiwid, and responded in very similar ways to a given treatment in the brown sand soils. Taken as a whole, the data indicated that N was the nutrient of major importance in the Tiwiwid sand while P was the nutrient which limited growth of pangolagrass on the brown sand soils. Additions of N and K to the latter soils also had beneficial effects.

Pigeon pea

The shoot weight variations of pigeon pea are shown in Table 27, and the responses to the added nutrients are summarized in Table 28. All responses were positive in the Kasarama soil, but those to S and K were negative in both the Tiwiwid and Tabela soils. In the Tiwiwid sand, responses to N and micronutrients were significant (Table 55), but micronutrient additions gave the largest response. In the Tabela soil, the positive responses to N, P, and micronutrients were all highly significant, as was the P response in the Kasarama soil. The N response in the latter soil was positive and significant. The data in Table 29

Table 26. --Root weights (oven-dried) of pangolagrass after two harvests.

Treatment	Soil			
	Tiwiwid	Tabela	Kasarama	Ebini
	g/pot			
Control	2.6	0.5	1.5	1.4
N	2.6	0.9	0.7	1.8
S	2.1	1.0	0.2	1.0
P	1.8	0.2	2.6	0.9
K	1.9	0.5	1.1	0.5
Tr	1.3	0.4	0.6	1.4
NS	0.2	0.5	0.9	1.4
NP	1.3	1.0	0.6	0.6
NK	2.1	1.0	0.9	1.3
NTr	1.7	0.4	0.5	0.3
SP	2.0	2.4	2.2	2.4
SK	4.3	1.1	0.7	0.3
STr	1.9	0.8	1.0	1.1
PK	3.4	0.1	1.2	1.4
PTr	1.3	2.4	2.2	1.9
KTr	1.9	0.6	1.6	1.4
NSP	1.1	0.6	1.2	1.1
MSK	1.9	1.0	1.7	1.2
NSTr	1.7	0.9	1.1	0.2
NPK	3.2	1.7	2.4	1.7
NPTr	1.7	0.7	1.2	0.2
NKTr	4.3	0.3	0.8	0.6
SPK	0.6	1.7	2.2	1.7
SPTr	1.4	2.2	2.4	0.8
SKTr	3.0	0.8	0.6	0.1
PKTr	2.5	3.0	2.0	1.6
NSPK	0.2	2.2	1.2	0.9
NSPTr	2.7	0.6	3.2	1.3
NSKTr	0.5	0.9	1.4	0.3
NPKTr	1.9	1.8	3.3	0.6
SPKtr	2.8	2.0	3.8	2.6
NSPKtr	3.4	1.2	2.9	0.1

Table 27. --Shoot weights (oven-dried) of pigeon pea.

<u>Treatment</u>	<u>Soil</u>		
	<u>Tiwiwid</u>	<u>Tabela</u>	<u>Kasarama</u>
	<u>g/pot</u>		
Control	4.0	0.6	0.7
N	4.5	0.7	0.7
S	3.8	0.6	0.6
P	4.6	3.7	1.9
K	4.2	0.5	0.8
Tr	5.0	0.8	1.0
NS	4.0	0.8	0.8
NP	6.4	4.3	2.7
NK	3.7	0.9	0.9
NTr	5.6	1.1	0.7
SP	4.9	2.2	2.0
SK	2.8	0.6	0.8
STr	5.2	0.8	1.0
PK	3.6	3.2	2.3
PTr	5.5	3.0	3.1
KTr	5.2	0.5	0.8
MSP	5.7	4.4	3.7
NSK	5.6	1.0	0.9
NSTr	6.3	0.9	0.8
NPK	4.4	3.3	4.6
NPTr	5.0	5.9	4.1
NKTr	6.9	0.9	0.9
SPK	4.3	3.6	4.3
SPTr	4.7	4.3	3.7
SKTr	3.8	0.8	0.9
PKTr	4.4	4.2	2.3
NSPK	2.7	3.6	2.7
NSPTr	6.7	5.3	5.5
NSKTr	2.6	0.8	0.5
NPKTr	6.6	6.1	5.9
SPKTr	4.2	3.9	2.9
NSPKTr	5.8	5.4	5.5

Table 28. —Shoot growth (oven-dried) of pigeon pea in response to fertilizer applications.

Soil	Treatment	Main effect			
		N	S	P g/pot	K
Tiwiwid sand	+	82.5	73.1	79.5	70.8
	-	70.2	79.6	73.2	81.9
	Response	12.3	-6.5	6.3	-11.1
	Slope	0.384	-0.203	0.197	-0.347
Tabela sand	+	45.4	39.0	66.4	39.3
	-	33.3	39.7	12.3	39.4
	Response	12.1	-0.7	54.1	-0.1
	Slope	0.378	-0.022	1.691	-0.003
Kaserama loamy sand	+	40.9	36.6	57.2	37.0
	-	29.1	33.4	12.8	33.0
	Response	11.8	3.2	44.4	4.0
	Slope	0.369	0.100	1.286	0.125

+ --Indicates the sum of yields of all pots supplied with fertilizer.

- -- " " " " " not supplied with fertilizer.

Table 29. --Root weights (oven-dried) of pigeon pea after one harvest.

<u>Treatment</u>	<u>Soil</u>		
	<u>Tiwiwid</u>	<u>Tabela</u> g/pot	<u>Kasarama</u>
Control	4.0	0.5	0.5
N	3.0	0.7	0.5
S	4.6	0.6	0.7
P	7.0	2.3	1.6
K	2.5	0.6	1.0
Tr	7.6	0.8	0.9
NS	1.2	0.9	0.7
NP	3.7	2.4	1.1
NK	2.3	0.7	0.7
NTr	5.6	0.8	0.4
SP	5.0	1.4	1.4
SK	1.7	0.6	0.6
STr	4.7	0.8	0.6
PK	2.6	2.0	1.9
PTr	4.5	1.9	1.8
KTr	3.1	0.5	0.6
NSP	5.2	2.6	2.6
NSK	4.7	0.7	0.5
NSTR	3.1	0.9	0.5
NPK	3.4	1.5	2.5
NPtr	4.2	2.4	1.7
NKTr	6.1	0.7	0.7
SPK	4.3	2.3	2.3
SPr	3.6	3.6	2.0
SKTr	4.2	0.7	0.7
PKTr	4.0	3.0	1.6
NSPK	1.3	2.1	1.1
NSPTr	4.4	3.2	2.3
NSKTr	1.1	0.6	0.3
NPKTr	4.3	4.0	2.6
SPKTr	2.0	2.2	1.3
NSPTr	3.2	2.3	2.0

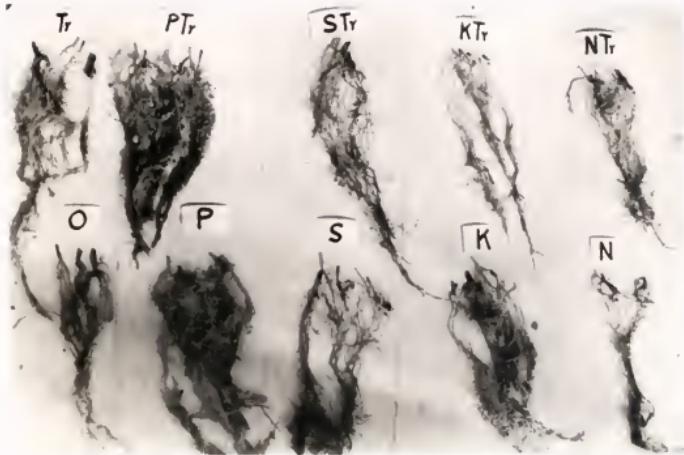
revealed that root weights, following the pattern of shoot weights, were highest in the Tiwiwid sand and that those in the Tabela and Kasarama soils were similar. In the latter soils, variations due to treatments were similar. Summaries of the responses in root growth are shown in Table 30. In the Tiwiwid soil, the responses to P and Tr were both positive, but only the negative effect of K was significant (Table 57). The K response was also negative, but not significant in the Tabela, as was the S response in the Kasarama soil. Responses to P and Tr were both positive and significant in the two brown sand soils.

The negative, though significant, effect of N in the Tiwiwid sand implied that in this soil nodulation was depressed by the action of added inorganic N on Rhizobial activity (287). The positive N responses on the Tabela and Kasarama soils suggested that N fixation was sub-optimal in the -N treatments in those soils. The sub-optimal level of N fixation was undoubtedly related to the steep slope of the P response in both of these soils. It was obvious that maximum nodulation occurred only after the addition of P and micronutrients (Fig. 8), and as has been reported, maximal nodulation was reflected by the size as well as number of the nodules formed (212). The effectiveness of those nodules which formed was dependent on the development of hemoglobin and, therefore, of a reddish coloration within the nodules (217). The absence of P and/or micronutrients, resulted in a reduction in size and in the degree of coloration of the nodules (Fig. 9).

Table 30. --Root growth (oven-dried) of pigeon pea in response to fertilizer applications.

Soil	Treatment	Main effect				
		N	S	P g./pot	K	T _R
Tiwivid sand	+	56.8	54.3	62.7	50.8	65.7
	-	65.4	67.9	59.5	71.4	56.5
	Response	-8.6	-13.6	3.2	-20.6	9.2
	Slope	-0.269	-0.425	0.100	-0.644	0.288
Tabela sand	+	26.5	25.5	39.2	24.5	28.4
	-	23.8	24.8	11.1	25.8	21.9
	Response	2.7	0.7	28.1	-1.3	6.5
	Slope	0.084	0.022	0.878	-0.041	0.203
Kasarama loamy sand	+	20.2	19.6	29.8	20.4	20.0
	-	19.5	20.1	9.9	19.3	19.7
	Response	0.7	-0.5	19.9	1.1	0.3
	Slope	0.022	-0.016	0.622	0.024	0.009

+ --Indicates sum of yields of all pots supplied with fertilizer
 - -- " " " " " not supplied with fertilizer



(a) Main effects and some first order interactions of added nutrients.



(b) Main effects and interactions of added P.

Fig. 8. --Effects of nutrient elements on the development of nodules on pigeon pea roots in Tabela sand.



(a) Main effects of added nutrients.



(b) Some main effects and interaction of added nutrients.

Fig. 9. --Effects of nutrient elements on the size and coloration of nodules developed by pigeon pea roots in Tabela sand.

Central Composite StudiesPangolagrass

The dry matter yields of pangolagrass on the three brown sand soils, resulting from various treatment combinations, are presented in Table 31. The omission of several treatment combinations permitted by the experimental design, dictated that treatments could best be described by regression coefficients. The coefficients obtained for each of the parameters when the model equation (201) was fitted to the dry matter yield data are shown in Table 32.

It is evident that in each soil there was a significant negative effect on yield induced by the addition of Ca, in contrast to a positive effect by the addition of P. The coefficient for P was appreciable but not significant in the Kasarama soil. Lack of significance was, however, apparently not due to a lesser effect of P on yield, but rather to the absence of any previous applications of P and the wider pH range utilized in this soil. The effect of K addition was negative and non-significant in the Tabela and Kasarama soils, but was positive and significant in the Ebini soil. The Ca^2 effect was also positive and significant in the last-named soil.

The fitted equations for the Tabela, Kasarama, and Ebini soils are diagrammatically represented in Fig. 10, 11, and 12, respectively, with computations based on the K level held constant at 100ppm. The figures show that at intermediate levels of P and K, yield decreased by some 10% from 9.2 to 8.3 g/pot as pH increased from 6.05 to 7.30 in the Tabela sand. In the Kasarama loamy sand, the yield dropped by approximately 57% from 15.7 to 6.7 g/pot as pH increased from

Table 31. --Dry matter yield of pangolagrass on the brown sand soils.

Soil	C ₂	Nutrients applied. P.D.M.					
		P		K		S/pot	
		39.25	50.00	100.00	150.00	100.75	150.00
Tabela sand	6.05	54.2	--	--	--	9.20	--
	6.20	80.0	--	11.37	8.70	--	--
	6.70	200.0	8.47	--	10.50	9.67	11.57
	7.10	320.0	--	7.47	6.23	6.63	12.80
	7.30	345.8	--	--	--	--	--
Kasarama loamy sand	4.90	179.8	--	--	--	8.33	9.70
	5.20	240.0	--	11.30	13.43	--	9.70
	6.10	520.0	8.40	--	12.17	--	--
	7.00	800.0	--	8.20	8.00	--	--
Ebini sandy loam	5.50	157.0	--	--	--	10.67	13.57
	5.65	200.0	--	8.60	10.03	--	--
	6.30	400.0	7.87	--	--	12.60	13.70
	7.00	600.0	--	7.40	8.83	--	--
	7.15	643.0	--	--	--	9.03	--

Table 32. --Comparison of the regression coefficients for dry matter yield (g/pot) of pangolagrass on the brown sand soils.

Variable	Estimated values and standard error of regression coefficients	
	Tabela	Kasarama Ebind
Mean	9.556000 ± 0.321823**	11.094000 ± 0.405940**
Ca	-1.131851 ± 0.376619**	-2.337737 ± 0.475052**
P	1.415511 ± 0.376619*	1.211473 ± 0.475052
K	-0.673981 ± 0.376619	-0.421943 ± 0.475052
Ca × P	0.175000 ± 0.440679	0.298750 ± 0.555855
Ca × K	0.025000 ± 0.440679	-0.758750 ± 0.555855
P × K	0.642500 ± 0.440679	-0.741250 ± 0.555855
Ca ²	-0.285098 ± 0.596856	0.184000 ± 0.752850
P ²	1.048586 ± 0.596856	-0.066489 ± 0.752850
K ²	-0.420497 ± 0.596856	0.556348 ± 0.752850

** and * significant at 99% and 95% probability levels, respectively.

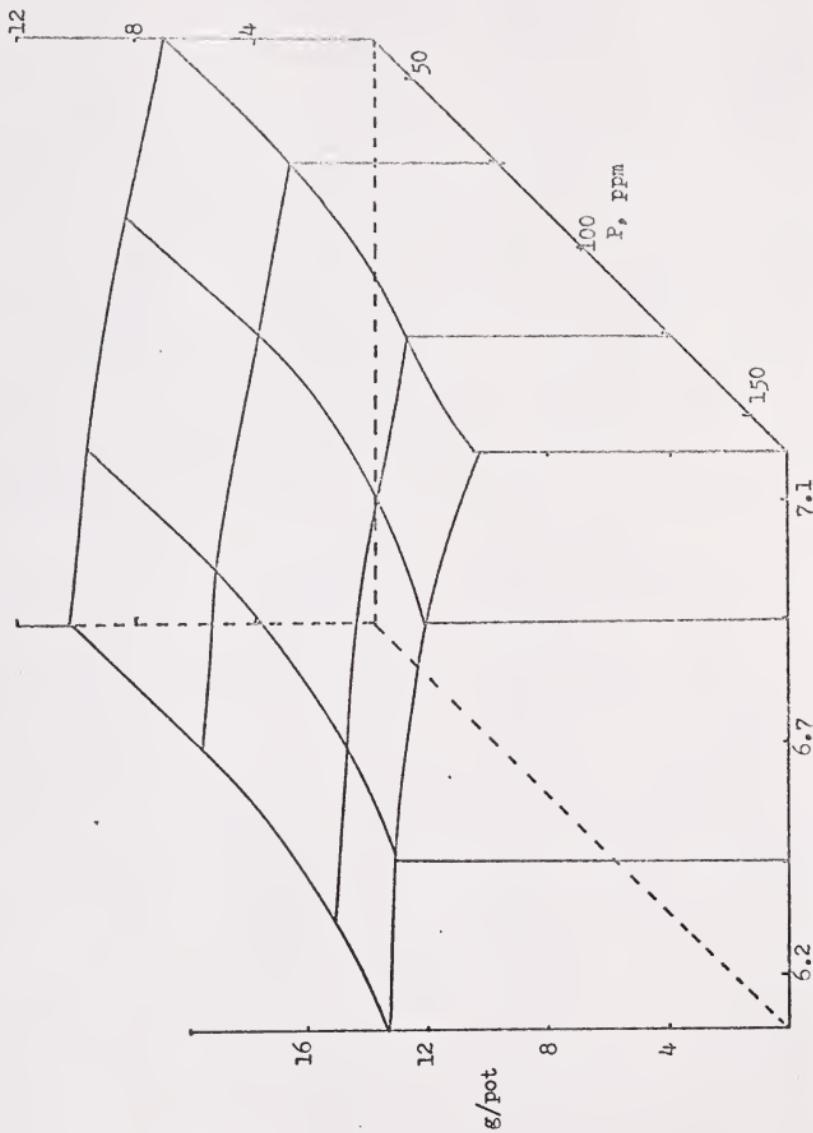


Fig. 10. --Dry matter yield of pangolagrass on Tabela sand.

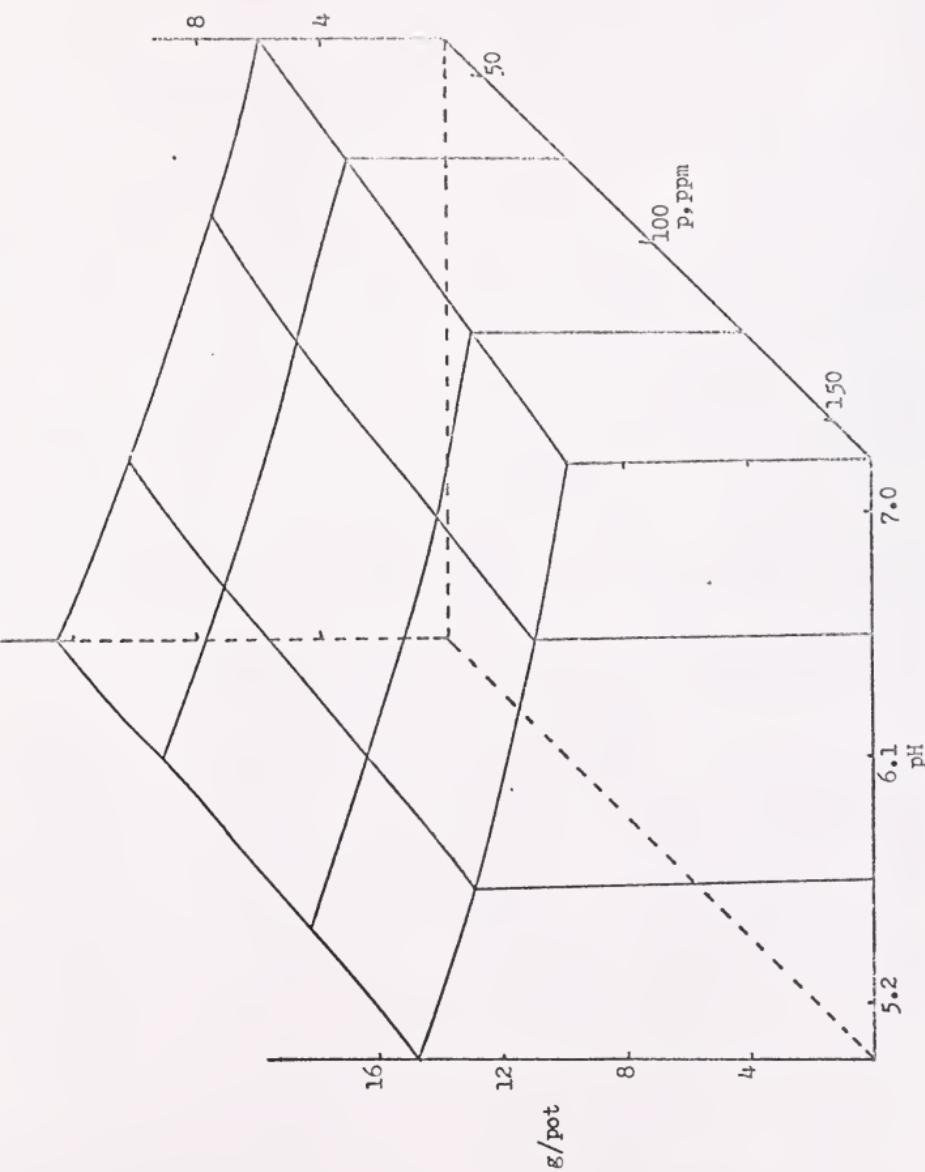


Fig. 11. --Dry matter yield of pangolagrass on Kasarama loamy sand.

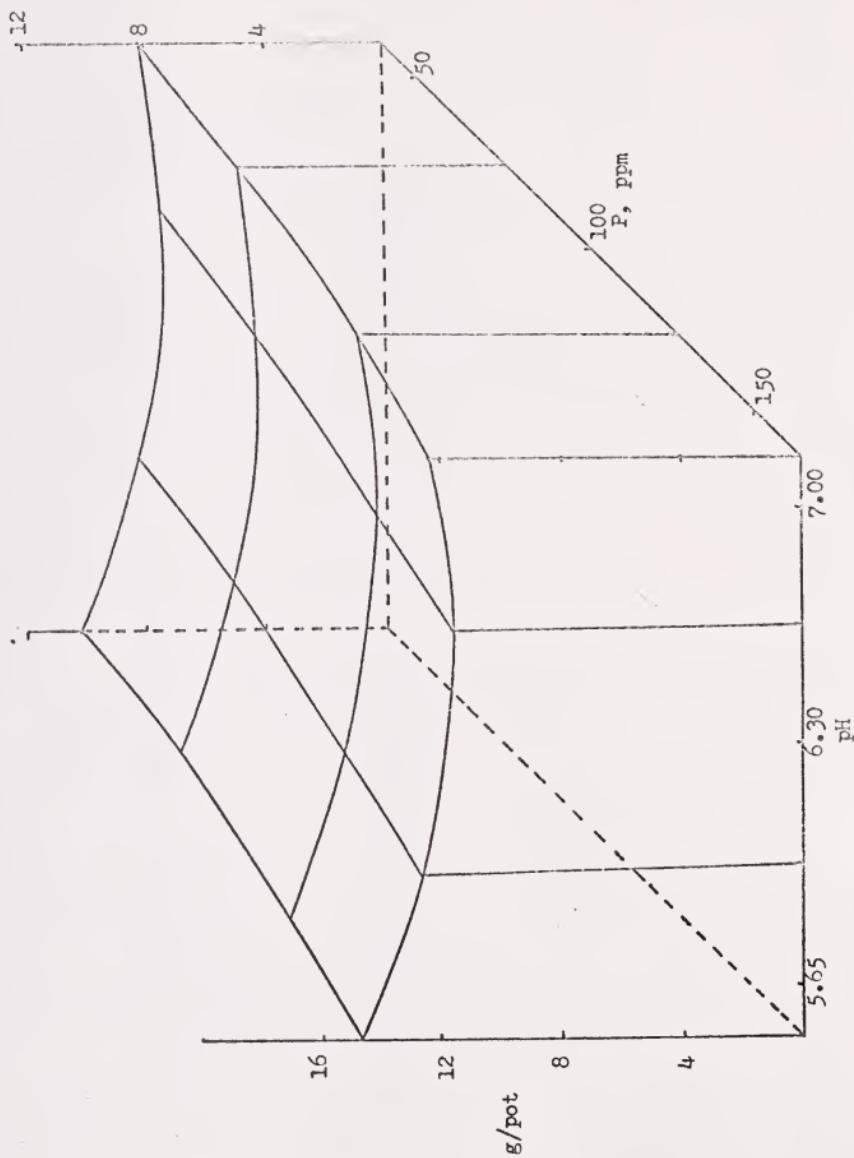


Fig. 12. —Dry matter yield of pangolagrass on Ebini sandy loam.

4.90 to 7.15, while a decrease of about 28% from 12.6 to 9.0 g/pot occurred as the pH of the Ebini sandy loam increased from 5.50 to 7.15. At intermediate levels of K and pH, the application of P resulted in yield increases of 54, 57, and 46% in the Tabela, Kasarama, and Ebini soils, respectively. The yield responses on the Tabela and Ebini soils were sizeable despite previous applications of 100ppm P to the soils in the experiment used to determine the limiting nutrients.

The negative effect of increasing pH on yield was more pronounced in terms of P concentration in the tissues of pangolagrass. Data in Table 33, showed that at low levels of P and K the concentration of P in the plant tissues increased somewhat with increase in pH; however, at high levels of P and K, increase in pH resulted in a decrease in P concentration. Similar trends were obtained for total P uptake as shown in Table 34. Coefficients of the fitted equations for P uptake (Table 35) reiterated the highly significant negative effects of pH, and the positive effects of P. The effect of K on P uptake varied, but was not significant. It was negative in the Tabela and Kasarama soils, but positive in the Ebini. The latter soil had a significant effect on P uptake due to the Ca x P interaction. Diagrammatic representations of the fitted equations for P uptake, at the 100ppm K level, from the Tabela, Kasarama, and Ebini soils are presented in Fig. 13, 14, and 15, respectively.

The surfaces for P uptake were strikingly similar to those for

Table 33. -Concentration of phosphorus in shoots of pangolagrass grown on the brown sand soils.

Soil	pH NKH	Nutrients applied, ppm									
		Ca		39.25		50.00		100.00		K	
		100.00	50.00	150.00	100.00	50.00	150.00	100.00	50.00	150.00	100.00
Tabala sand	6.05	54.2	--	--	--	--	--	0.294	--	--	--
	6.20	80.0	--	0.176	0.195	--	--	0.290	0.276	--	--
	6.70	200.0	0.166	--	--	0.252	0.244	0.274	--	--	0.264
	7.10	320.0	--	0.174	0.182	--	--	0.254	0.238	--	--
	7.30	345.8	--	--	--	--	0.244	--	--	--	--
Kasarema loamy sand	4.90	179.8	--	0.146	--	--	0.180	--	--	--	--
	5.20	240.0	--	0.176	0.154	--	--	0.192	0.212	0.244	--
	6.10	520.0	--	--	--	0.177	0.204	--	--	--	0.218
	7.00	800.0	--	0.152	0.154	--	--	0.198	--	0.200	0.186
	7.15	860.2	--	--	--	--	--	--	--	--	--
Ebin sandy loam	5.50	157.0	--	--	--	--	0.173	--	--	--	--
	5.65	200.0	--	0.152	0.156	--	--	0.224	0.172	--	--
	6.30	400.0	0.156	--	--	0.188	0.166	0.164	--	--	--
	7.00	600.0	--	0.162	0.170	--	--	0.156	0.172	0.218	--
	7.15	643.0	--	--	--	--	0.160	--	--	--	--

Table 34. --Total uptake of phosphorus by pangolagrass from the brown sand soils.

Soil	pH NKCl	Ca 100.00	Nutrients applied, ppm					
			P			K	100.00	150.00
			39.25 50.00 100.00	39.25 50.00 150.00	39.25 100.00 160.75	Mg/pot	50.00	150.00
Tabelia sand	6.05	108.4	--	--	--	27.0	--	--
	6.20	160.0	--	20.0	17.0	--	33.6	35.3
	6.70	400.0	14.1	--	26.5	23.6	--	--
	7.10	640.0	--	13.0	11.3	--	24.6	23.1
	7.30	691.6	--	--	--	18.7	--	--
Kassarama loamy sand	4.90	359.6	--	--	--	28.2	--	--
	5.20	480.0	--	16.5	20.7	--	29.0	30.4
	6.10	1040.0	14.8	--	22.6	19.8	20.5	--
	7.00	1600.0	--	12.5	12.3	--	25.0	28.8
	7.15	1720.4	--	--	--	13.2	--	--
Ebirri sandy loam	5.50	314.0	--	--	--	21.8	--	--
	5.65	400.0	--	13.1	16.7	--	26.8	25.0
	6.30	800.0	12.3	--	16.0	16.3	15.9	--
	7.00	1200.0	--	12.0	15.0	--	--	25.0
	7.15	1286.0	--	--	--	14.5	--	--

Table 35. --Comparison of the regression coefficients for total uptake of phosphorus (g/pot) by pangolagrass from the brown sand soils.

Variable	Estimated values and standard error of regression coefficients	
	Tabela	Kasarama
Mean	0.022687 ± 0.000600**	0.020693 ± 0.000516**
Ca	-0.004016 ± 0.000702**	-0.004467 ± 0.000604**
P	0.007290 ± 0.000702**	0.005068 ± 0.000604**
K	-0.001332 ± 0.000702	-0.000552 ± 0.000604
Ca x P	-0.001063 ± 0.000821	-0.000738 ± 0.000707
Ca x K	-0.000238 ± 0.000821	-0.001838 ± 0.000707
P x K	0.000613 ± 0.000821	-0.001438 ± 0.000707
Ca ²	-0.000713 ± 0.001112	-0.000694 ± 0.000958
P ²	0.000200 ± 0.001112	0.000051 ± 0.000958
K ²	-0.001052 ± 0.001112	-0.000119 ± 0.000958
Ebin1		

** and * significant at 99% and 95% probability levels, respectively.

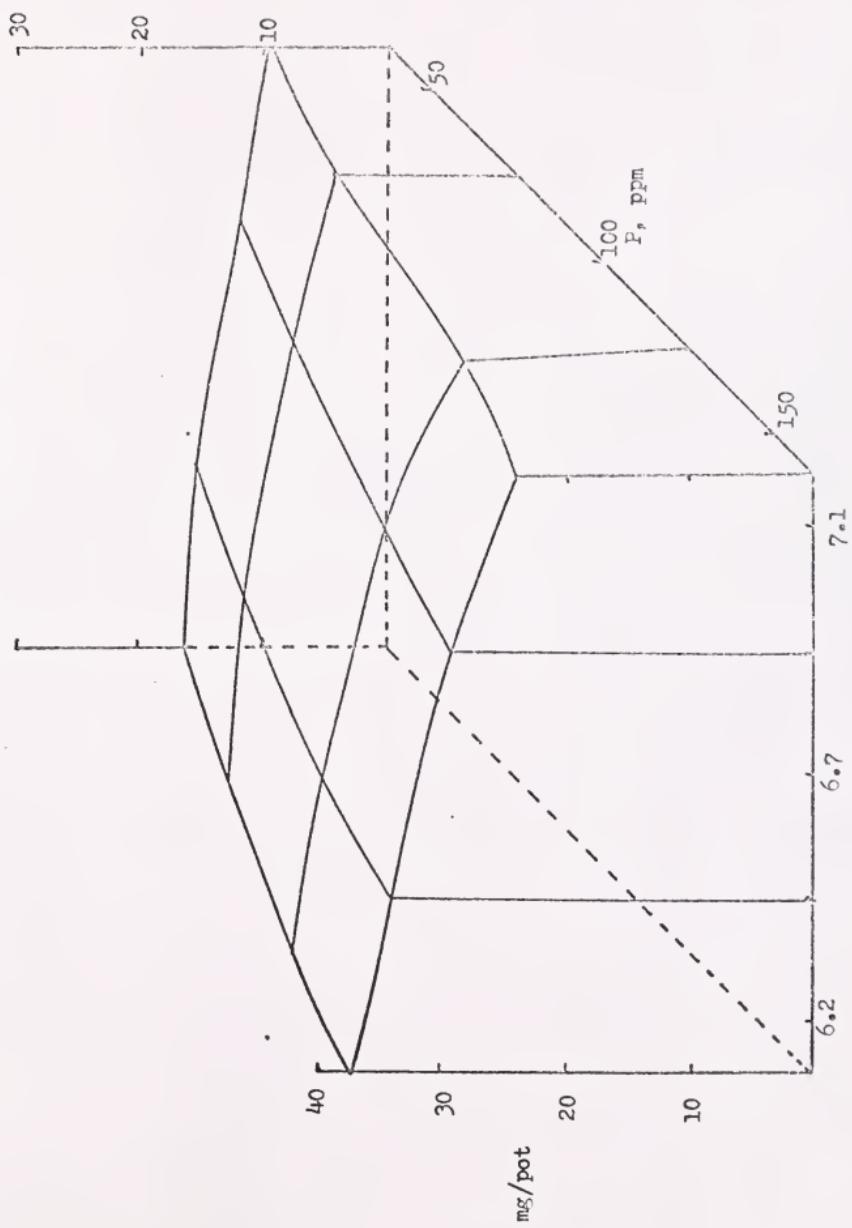


Fig. 13. --Phosphorus uptake from Tabela sand.

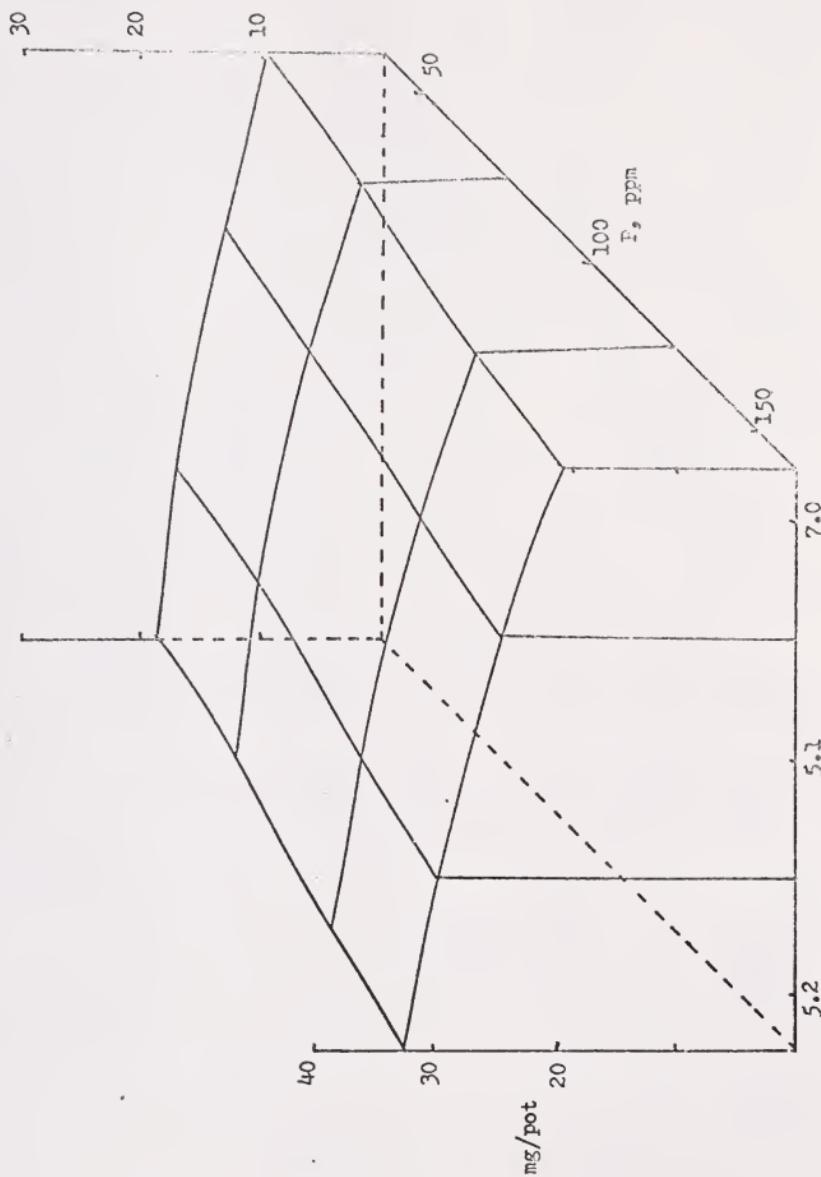


FIG. 14. — Phosphorus uptake from Kasarama loamy sand.

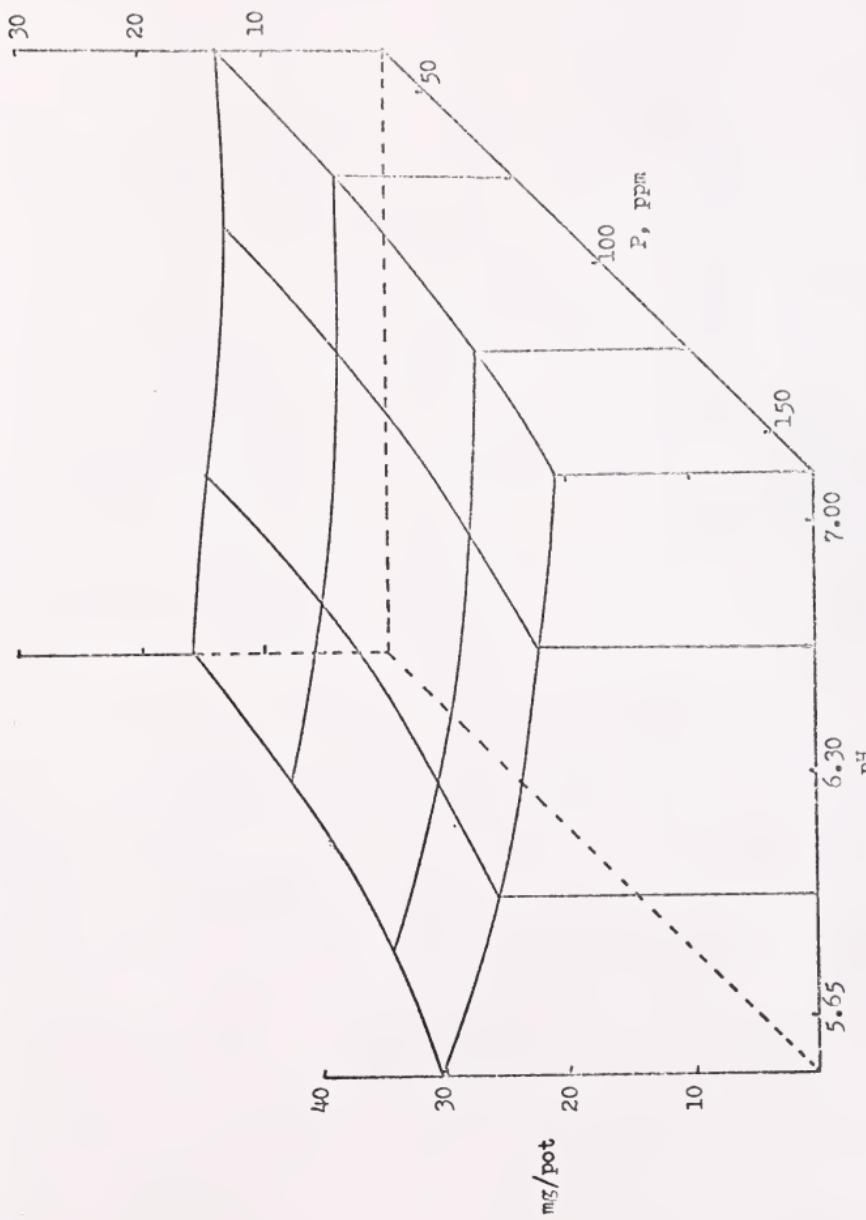


Fig. 15. --Phosphorus uptake from Ebinini sandy loam.

dry matter yields, emphasizing the importance of the supply of P for plant growth on the soils. The negative effect of increasing pH would appear to be due to the decreased solubility of the compounds formed on the addition of P to these soils. This is consistent with the effects of $\text{pH} > 5$ on complexes of the form $\text{P-(Al, Fe)-fulvic acids}$ (168).

The concentration of Ca in the pangolagrass tissues increased with increase in pH (Table 36). The coefficients for the Ca uptake equation, shown in Table 37, indicated that pH had no real effect on Ca uptake. The effects of P on Ca uptake were positive but significant only in the Ebini soil; K exerted a negative influence in the Tabela and Kasarama soils. The non-significance of the coefficients for Ca and K in each of the soils, and for P on two soils indicated that the supply of Ca was adequate at all pH levels, and that the release of Ca to the plant roots by the soil did not depend, to any appreciable extent, on the degree of Ca-saturation of the soil.

The data in Table 38 indicate that the concentration of Mg in the tissues was depressed by increase of pH and P levels. The uptake of Mg, as shown in Table 39, was subject to a significant negative effect from increased pH. The effects of P addition were positive but significant only in the Ebini sandy loam. Increase in the K level exerted a negative effect which attained significance in the Tabela sand only. The high degree of solubility of Mg at high pH values suggested that Mg uptake would be enhanced by increasing the

Table 26. --Concentration of calcium in shoots of pangolagrass grown on the brown sand soils.

Soil	P^{H} MgCl ₂	Nutrients applied, ppm						100.75	
		Ca		P		K			
		39.25	50.00	50.00	150.00	39.25	100.00		
Tabela sand	6.05 6.20 6.70 7.10 7.30	54.2 80.0 200.0 320.0 345.8	-- -- 0.425 0.500 --	-- -- 0.400 0.450 --	-- -- 0.500 -- --	0.375 0.425 0.425 0.500 0.500	-- -- 0.425 0.425 --	0.400 0.425 0.425 0.450 --	
Kasarama loamy sand	4.90 5.20 6.10 7.00 7.15	179.8 240.0 620.0 800.0 350.0	-- -- 0.260 0.500 --	-- 0.425 0.575 0.560 --	-- 0.425 0.575 0.400 0.625	0.350 0.400 0.400 0.560 --	-- 0.425 0.460 0.560 --	0.325 0.325 0.475 0.475 --	
Ebini sandy loam	5.50 5.65 6.20 7.00 7.15	157.0 200.0 400.0 600.0 643.0	-- -- 0.400 0.475 --	-- 0.375 0.490 0.500 0.450	-- 0.400 0.400 0.450 --	0.350 0.400 0.400 0.500 --	-- 0.350 0.400 0.500 --	-- 0.340 0.460 0.400 --	

Table 37. --Comparison of the regression coefficients for total uptake of calcium (g/pot) from the brown sand soils.

Variable	Estimated values and standard error of regression coefficients		
	Tabela	Kasazawa	Ebin ¹
Mean	0.040427 ± 0.001880**	0.050820 ± 0.002224**	0.042573 ± 0.001366**
Ca	-0.001091 ± 0.002200	-0.001188 ± 0.002602	0.001575 ± 0.001599
P	0.004825 ± 0.002200	0.004076 ± 0.002602	0.006288 ± 0.001599*
K	-0.004987 ± 0.002200	-0.005352 ± 0.002602	0.000370 ± 0.001599
Ca × P	0.001838 ± 0.002574	0.001813 ± 0.003045	0.000838 ± 0.001871
Ca × K	0.001413 ± 0.002574	-0.004213 ± 0.003045	-0.001713 ± 0.001871
P × K	0.002588 ± 0.002574	-0.007138 ± 0.003045	-0.002038 ± 0.001871
Ca ²	-0.002060 ± 0.003486	-0.002533 ± 0.004124	0.001571 ± 0.002524
R ²	0.001630 ± 0.003496	-0.001025 ± 0.004124	0.002080 ± 0.002534
R ²	-0.000536 ± 0.003486	0.006268 ± 0.004124	-0.000116 ± 0.002534

** and * significant at 99% and 95% probability levels, respectively.

Table 38. --Concentration of magnesium in shoots of pangolagrass grown on the brown sand soils.

Soil	pH NKCl	C ₂	Nutrients applied, ppm							
			P		K		150.00		100.75	
			39.25	50.00	100.00	150.00	39.25	100.00	160.75	50.00
Tabela sand	6.05	54.2	--	--	0.330	0.270	--	0.315	--	--
	6.20	80.0	--	--	0.270	0.350	--	0.295	0.260	--
	6.70	200.0	--	--	0.320	0.285	--	0.300	--	0.270
	7.10	320.0	--	--	0.320	0.285	--	0.320	0.280	0.235
	7.30	345.8	--	--	--	--	--	--	--	--
Kasararama loamy sand	4.90	179.8	--	--	0.325	0.235	--	0.225	--	--
	5.20	240.0	--	--	0.265	0.265	--	0.225	0.250	0.205
	6.10	520.0	--	--	0.255	0.255	--	0.200	0.250	--
	7.00	800.0	--	--	--	--	--	0.245	--	0.215
	7.15	860.2	--	--	--	--	--	--	--	--
Ebinai sandy loam	5.50	157.0	--	--	--	--	0.250	--	--	--
	5.65	200.0	--	--	0.320	0.255	--	--	0.285	0.215
	6.30	400.0	--	--	0.270	0.250	--	0.270	0.250	--
	7.00	600.0	--	--	0.250	0.260	--	--	0.240	0.205
	7.15	643.0	--	--	--	--	0.240	--	--	--

Table 39. --Comparison of the regression coefficients for total uptake of magnesium (g/pot) by pangolagrass from the brown sand soils.

Variabell	Estimated values and standard error of regression coefficients		
	Tabela	Kasarama	Ebinl
Mean	0.027840 ± 0.001155**	0.027527 ± 0.001155**	0.026487 ± 0.000462**
Ca	-0.003606 ± 0.001351*	-0.005842 ± 0.001351**	-0.003351 ± 0.000540**
P	0.002695 ± 0.001351	0.001246 ± 0.001351	0.003291 ± 0.000540**
K	-0.004185 ± 0.001351*	-0.003469 ± 0.001351	-0.000853 ± 0.000540
Ca × P	0.000238 ± 0.001581	0.001738 ± 0.001581	-0.000200 ± 0.000632
Ca × K	0.000536 ± 0.001581	-0.000688 ± 0.001581	0.000625 ± 0.000632
P × K	0.001863 ± 0.001581	-0.001483 ± 0.001581	-0.001225 ± 0.000632
Ca ²	-0.000594 ± 0.002141	-0.001241 ± 0.002141	0.000101 ± 0.000856
P ²	0.000185 ± 0.002141	-0.000225 ± 0.002141	0.000135 ± 0.000856
K ²	-0.000255 ± 0.002141	0.003295 ± 0.002141	-0.000204 ± 0.000856

** and * significant at 99% and 95% probability levels, respectively.

soil pH; however, the solubility of Ca also increased with increase in pH, and this permitted greater competition between the ions for uptake by plant roots. The larger quantities of Ca in the soil solution could thus decrease the activity and uptake of Mg. The positive effect of P may have been a consequence of improved growth consequent on the addition of P to the soils. The greater quantity and solubility of K in the soils probably increased competition between the cations for absorption sites on the plant roots and were thereby responsible for the negative K effect.

The concentration of K increased with increases in the levels of K and pH, but decreased at high levels of P, as shown in Table 40. The increase in K concentration with increases in pH was probably the combined result of reduced growth and enhanced solubility of K at higher pH levels. The increase in K concentration with increased supply of K was undoubtedly due to the greater amounts of K in the soil solution which resulted from this treatment. The decrease in K concentration seen at higher P levels was possibly a consequence of the sorption of K with P. The uptake of K suffered a negative pH effect in each soil, but this was only significant in the Kasarama soil (Table 41). The P effect was positive in each soil but was not significant in the Kasarama soil, while the K effect was positive and highly significant in each case. The interaction of Ca x P exerted a significant effect in the Kasarama and Ebini soils but this was negative in the Ebini. Similarly, the Ca x K interaction was highly significant in the

Table 40. --Concentration of potassium in shoots of pangolagrass grown on the brown sand soils.

Soil	pH NKCl	Nutrients applied, ppm						150.00 50.00	100.00 100.00	100.75 150.00			
		Ca		P		K							
		39.25 100.00	50.00 50.00	50.00 150.00	39.25 100.00	100.00 160.75	50.00 50.00						
<hr/>													
Tabelia sand	6.05	54.2	--	--	2.78	--	2.20	--	--	--			
	6.20	80.0	--	1.25	--	--	--	1.23	2.47	--			
	6.70	200.0	2.33	--	1.10	2.35	2.53	--	--	1.67			
	7.10	320.0	--	1.68	2.92	--	--	1.42	2.60	--			
	7.30	345.8	--	--	--	2.42	--	--	--	--			
Kasarama loamy sand	4.90	179.8	--	--	1.37	--	1.60	--	--	--			
	5.20	240.0	--	2.23	2.45	--	--	1.02	2.05	--			
	6.10	520.0	--	1.60	--	1.10	2.41	2.72	--	1.60			
	7.00	800.0	--	--	2.57	--	--	1.33	2.45	--			
	7.15	860.2	--	--	--	2.57	--	--	--	--			
Ebinu sandy loam	5.50	157.0	--	--	--	1.72	--	--	--	--			
	5.65	200.0	--	1.42	1.85	--	--	1.64	2.03	--			
	6.20	400.0	2.32	--	1.32	1.98	2.74	--	--	2.00			
	7.00	600.0	--	1.65	2.82	--	--	1.10	2.55	--			
	7.15	643.0	--	--	--	2.15	--	--	--	--			

Table 41. --Comparison of the regression coefficients for total uptake of potassium (g/pot) from the brown sand soils.

Variable	Estimated values and standard error of regression coefficients	
	Tabelia Kasarema	Ebini
Mean	0.195667 ± 0.001655**	0.206753 ± 0.002115**
Ca	-0.013346 ± 0.005447	-0.025888 ± 0.003997**
P	0.016519 ± 0.005447*	0.000373 ± 0.003997
K	0.053237 ± 0.005447**	0.056065 ± 0.003997**
Ca x P	0.001000 ± 0.006373	0.013250 ± 0.001677*
Ca x K	-0.012850 ± 0.006373	-0.024150 ± 0.004677**
P x K	0.016525 ± 0.006373*	-0.008125 ± 0.004677
Ca ²	-0.001567 ± 0.008632	-0.005764 ± 0.006334
P ²	0.001987 ± 0.008632	-0.013753 ± 0.006334
K ²	-0.020015 ± 0.008632	-0.002853 ± 0.006334

** and * significant at 99% and 95% probability levels, respectively.

Kasarama and Ebini soils, but was negative in the Tabela and Kasarama. The P x K interaction exerted a positive and significant effect in the Tabela and Ebini, and a negative effect in the Kasarama soil.

Table 42 shows that the concentration of N in the tissues tended to decrease with increase in pH, K, and P. Uptake of N (Table 43) was subject to a highly significant negative Ca effect, and to a positive P effect. The P effect was highly significant in the Tabela and Ebini soils. The effect of K on N uptake varied. It was significant in the Tabela and Ebini soils, but negative in the Tabela and Kasarama. The effects of the Ca x K and P x K interactions and of the P^2 and K^2 terms were significant in the Tabela soil only, with the Ca x K interaction and the K^2 effects being negative. The depression of N concentration at higher pH levels was probably due to competition between Ca and N, with Ca uptake being facilitated by the higher amount of Ca in the soil solution. A similar explanation probably applies to the K effect, while the P effect may have been due to dilution concomitant with the greater growth of the plants at constant N and higher P levels. The uniformity of color in the plants was perhaps indicative of better utilization of N at the higher pH levels (205).

The effects of acidity on plant growth are usually attributed to high levels of activity of H^+ and/or to Al toxicity (114, 241). In the pH ranges used in this study, H^+ should have been largely neutralized (274), leaving Al as the factor most likely to be active.

Table 42. --Concentration of nitrogen in shoots of pangolagrass grown on the brown sand soils.

Soil	pH NKCl	Ca 100.00	Nutrients applied, ppm					
			P		K		N	
			39.25 50.00 100.00	100.00 150.00 200.00	39.25 100.00 150.00	100.00 150.00 200.00	160.75 50.00 100.00	150.00 150.00 100.00
Tabela sand	6.05	54.02	--	--	--	1.86	--	--
	6.20	80.0	--	1.42	1.79	--	--	--
	6.70	200.0	1.68	--	--	1.45	1.52	1.52
	7.10	320.0	--	1.67	1.57	--	1.52	1.41
	7.30	345.8	--	--	--	--	1.53	--
Kasarama loamy sand	4.90	179.8	--	--	--	1.37	--	--
	5.20	240.0	--	1.79	1.59	--	1.48	1.57
	6.10	520.0	1.85	--	1.74	1.75	--	--
	7.00	800.0	--	1.55	1.57	--	1.65	1.46
	7.15	860.2	--	--	--	1.69	--	--
Ebinu sandy loam	5.50	157.0	--	--	--	1.57	--	--
	5.65	200.0	--	1.84	1.54	--	--	--
	6.20	400.0	1.67	--	--	1.75	1.50	1.44
	7.00	600.0	--	1.56	1.62	--	--	--
	7.15	643.0	--	--	--	1.42	--	--

Table 43. --Comparison of the regression coefficients for total uptake of nitrogen (g/pot) from the brown sand soils.

Variable	Tabela	Kaserzana	Ebin ¹
Mean	0.150627 ± 0.001528**	0.174840 ± 0.004066**	0.159160 ± 0.002452**
Ca	-0.019942 ± 0.001788**	-0.037273 ± 0.004758**	-0.021493 ± 0.002873**
P	0.016506 ± 0.001788**	0.008035 ± 0.004758	0.019070 ± 0.002873**
K	-0.005452 ± 0.001788*	-0.005175 ± 0.004758	0.007721 ± 0.002873*
Ca x P	0.002398 ± 0.002992	0.005350 ± 0.005568	-0.005125 ± 0.003362
Ca x K	-0.006263 ± 0.002092*	-0.005650 ± 0.005568	0.005450 ± 0.003362
P x K	0.0005113 ± 0.002292*	-0.002675 ± 0.005568	0.002425 ± 0.003362
Ca ²	0.000761 ± 0.002083	-0.011924 ± 0.007541	0.004892 ± 0.004553
P ²	0.009629 ± 0.002083*	-0.004849 ± 0.007541	0.002999 ± 0.004553
K ²	-0.006652 ± 0.002083*	0.012076 ± 0.007541	-0.000590 ± 0.004553

** and * significant at 99% and 95% probability levels, respectively.

The data in Table 44 indicated that despite the visually normal growth of the roots, substantial amounts of Al were associated with them. The data revealed no obvious trends in the amounts of Al in relation to changes in pH; however, increasing levels of K decreased the amounts of Al in the roots. This may have been due to the formation of insoluble K-Al-P compounds (295) which reduced the amounts of mobile Al in the soil. This possibility is supported by similar, but less marked, reduction of root P by increased K levels as shown in Table 45. These data also show that concentration of P in the root increased with increase in pH. The Al:P ratios presented in Table 46 were narrower at higher pH levels in the Ebini and Kasarama soils suggesting that more P might have been immobilized by Al in or on the roots (333, 334) at higher pH levels. The tendency for the ratios to have values of about 3 to 4 indicated the possible formation of Al-P compounds in the roots (60). The inconsistent effects of K on the Al/P ratios probably reflected differences in the amounts of P sorbed in the soil as potassium phosphate salts (207) and, therefore, in the degree to which the P sorption capacity of each soil was satisfied. The absence of any really overwhelming trends in the Al relations in the root system, seems to imply that the effects of pH increases on plant growth were related more to changes in soil properties than to impaired plant metabolism.

Pigeon pea

Pigeon pea plants, grown on both the Tiwiid and Kasarama soils, developed necrotic areas on the lower leaves soon after abscission of the cotyledons. The necrosis began at the apex of the older leaves,

Table 44. - Concentration of aluminum in roots of pangolagrass grown on the brown sand soils.

Soil	pH NKCCL	Nutrients applied, ppm									
		Ca			Mg			K			
		39.25	50.00	100.00	50.00	150.00	39.25	100.00	169.75	50.00	150.00
Tabela sand	6.05	54.2	--	--	2600	1100	--	--	1475	--	--
	6.20	80.0	--	--	--	--	--	--	2035	1500	--
	6.70	200.0	1375	--	--	1970	1775	1650	--	--	1325
	7.10	320.0	--	2275	2050	--	--	--	1775	1600	--
	7.30	345.8	--	--	--	--	1725	--	--	--	--
Kasararama loamy sand	4.90	179.8	--	--	--	--	1475	--	--	--	--
	5.20	240.0	--	1005	2100	--	--	--	1425	2100	--
	6.10	520.0	1235	--	--	2000	2425	1825	--	--	1650
	7.00	800.0	--	2825	1375	--	--	--	1275	1010	--
Ebini sandy loam	7.15	860.2	--	--	--	--	1010	--	--	--	--
	5.50	157.0	--	--	--	--	2000	--	--	--	--
	5.65	200.0	--	2500	2100	--	--	--	3000	2325	--
	6.20	400.0	2675	--	--	2325	2150	2375	--	--	1600
	7.00	600.0	--	2100	1325	--	--	--	2050	2450	--
	7.15	643.0	--	--	--	--	--	1875	--	--	--

Table 45. --Concentration of phosphorus in roots of pangolagrass as affected by the addition of nutrients to the soil.

Soil	pH NKCl	Nutrients applied. ppm					
		Ca		P		K	
		39.25 100.00	50.00 50.00	100.00 150.00	39.25 100.00	100.00 150.00	150.00 160.75
Tabala sand	6.05 6.20 6.70 7.10 7.30	54.2 80.0 200.0 320.0 345.8	-- -- 0.019 0.012 --	-- -- 0.018 0.026 --	-- -- 0.034 0.032 0.026	-- -- 0.038 0.030 --	-- -- 0.034 0.030 --
Kasarama loamy sand	4.90 5.20 6.10 7.10 7.15	179.8 240.0 520.0 800.0 860.2	-- -- 0.028 0.028 --	-- 0.026 0.043 0.026 0.043	-- 0.028 0.028 0.026 0.043	-- 0.043 0.038 0.038 --	-- 0.036 0.036 0.047 --
Ebinif sandy loam	5.50 5.65 6.30 7.00 7.15	157.2 200.0 400.0 600.0 643.0	-- -- 0.024 0.035 --	-- 0.038 0.045 0.032 0.048	-- 0.047 0.047 0.048 0.048	-- 0.037 0.037 0.028 --	-- 0.040 0.040 0.028 0.044

Table 46. --Ratios of Al:P in pangolagrass roots as affected by added nutrients.

Soil	pH NKC1	Nutrients applied, ppm									
		Ca		P		K		Mg		Zn	
		39.25	50.00	100.00	150.00	38.25	100.00	160.75	50.00	150.00	100.00
Tabela sand	6.05	54.02	--	13.68	6.11	--	4.24	--	17.14	4.41	--
	6.20	80.0	--	--	--	--	--	--	--	--	--
	6.70	200.0	5.29	--	--	5.47	5.55	4.24	--	--	3.49
	7.10	320.0	--	9.48	17.08	--	--	--	5.92	12.20	--
	7.30	345.8	--	--	--	--	6.63	--	--	--	--
Kasarama loamy sand	4.90	179.8	--	--	--	--	5.67	--	--	--	--
	5.20	240.0	--	2.59	8.08	--	--	--	3.31	5.84	--
	6.10	520.0	4.41	--	--	4.65	8.66	4.24	--	--	4.58
	7.00	800.0	--	10.09	5.29	--	--	--	3.36	2.45	--
	7.15	860.2	--	--	--	--	2.35	--	--	--	--
Ebini sandy loam	5.50	157.2	--	--	--	--	4.76	--	--	--	--
	5.65	200.0	--	10.42	5.53	--	--	--	7.50	7.50	--
	6.20	400.0	8.11	--	--	5.17	4.57	6.42	--	--	3.72
	7.00	600.0	--	6.00	4.14	--	--	--	10.89	5.57	--
	7.15	643.0	--	--	--	--	3.91	--	--	--	--

and the affected areas expanded along the margins towards the leaf base and inwards to the midrib. The dried margins curled downwards and inwards shortly before the premature abscission of the affected leaves. The symptoms bore some similarities to those described by Nichols (212) for K and Mg deficiencies, but showed no variations in severity, and were alleviated by neither the addition of 40ppm Mg to each pot, nor the foliar application of each of the micronutrients.

The heavy leaf fall during the study rendered the dry weights of the plants little more than inaccurate estimates of dry matter production. In addition to the problem of leaf fall, the soil pH levels after harvest varied considerably from those anticipated. The lowest lime treatment on the Kasarama soil resulted in a final pH which was very close to that produced by the highest level of lime. This similarity in pH was very likely due to incorrect mixing of the limed and unlimed soils in this particular case.

The dry weights of pigeon pea attributable to the different treatments are shown in Table 47. The plants grown on the Tiwiwid sand showed a very positive response to increased Ca supply, while responses to P and K increased to a maximum and then decreased. Plants grown on the Kasarama soil, ignoring those of the pH 6.10 treatment, seemed to have responded positively to increased P and negatively to increased K.

The concentration of P (Table 48) in the plant material from the Tiwiwid soil, increased to a maximum and then declined as the P supply was increased (at the 100ppm K level). There seemed to be no appreciable effect due to K, but P concentration was lowered

Table 47. --Dry matter yield of pigeon pea in relation to nutrient supply.

Soil	pH NKC1	ppm	Nutrients applied, ppm										
			Ca		P		K						
			39.25	50.00	50.00	150.00	32.25	100.00	32.25	100.00	50.00	150.00	100.00
Tiliwid sand	6.35	54.2	-	-	4.23	-	4.07	-	-	3.50	3.57	-	-
	6.45	80.0	-	3.97	-	-	-	-	-	-	-	-	-
	6.80	200.0	5.63	-	-	5.17	6.23	4.10	-	-	-	-	4.40
	7.15	320.0	-	6.43	5.23	-	-	-	-	4.53	5.40	-	-
	7.45	345.8	-	-	-	-	5.20	-	-	-	-	-	-
Kasarama loamy sand	6.10	54.2	-	-	3.20	3.07	-	4.23	-	-	3.83	2.60	-
	6.20	80.0	-	-	-	-	-	-	-	-	-	-	-
	6.60	200.0	3.50	-	-	3.87	3.80	3.23	-	-	-	-	5.13
	6.95	320.0	-	3.30	2.67	-	-	-	-	4.13	3.83	-	-
	7.10	345.8	-	-	-	-	3.63	-	-	-	-	-	-

Table 48. --Concentration of phosphorus in pigeon pea as affected by the addition of nutrients to the soil.

Soil	pH NKCl ppm	Ca 39.25 100.00 %	P 50.00 50.00 150.00 %	Nutrients applied, ppm								
				K			100.00			150.00		
				39.25	100.00	160.75	50.00	100.00	160.75	50.00	100.00	150.00
Tinwald sand	6.35 6.45 6.80 7.15 7.45	54.2 80.0 200.0 320.0 345.8	- - 0.17 0.15 -	0.26 0.18 - 0.16 -	- - 0.22 - -	0.29 - 0.25 - 0.35	- - 0.23 - -	- - 0.26 - 0.10	- 0.31 - 0.25 -	- 0.31 - 0.25 -	- - 0.21 - -	
Kassarama loamy sand	6.10 6.20 6.60 6.95 7.10	54.2 80.0 200.0 320.0 345.8	- - 0.09 - -	0.11 - 0.11 0.12 -	0.12 - 0.10 0.12 -	0.11 - 0.09 - -	- - 0.12 - 0.10	- 0.12 - 0.12 -	- 0.12 - 0.12 -	- 0.13 - 0.12 -	- 0.11 - 0.12 -	

by increased pH. In the plants grown on the Kasarama soil, the concentration of P was influenced to a very small degree only. The major effect was positive and due to K, while pH and P increases exerted very little effect.

Table 49 shows the concentrations of Ca, Mg, and K in the tissues of plants grown on the Tiwiwid sand. The concentration of Ca increased with increase in P level, but was not affected greatly by changes in pH. The concentration of Mg also increased with increases in P, but decreased as K and pH levels increased. Increases in P and K levels increased the concentration of K. Plants grown on the Kasarama soil showed a positive effect of K on Ca concentration (Table 50) at low P levels. Increasing P levels depressed the Ca concentration as compared to the increases which resulted from increases in K and pH. The concentration of Mg was increased by increasing the K level, but was not greatly affected by increases in pH and in P supply. Increasing the K levels increased the K concentration in the plants, while increasing pH and P levels decreased it.

Except for the Ca concentration in plants grown on the Tiwiwid sand at low P levels, the concentrations of the cations were very similar in plants from both soils. The levels of 0.44% Mg and 1.85% Ca, regarded as adequate (212), were not met by the plants on either soil, though the concentration of 0.25%, regarded as the point of incipient Mg deficiency was generally exceeded. The K concentrations in all plants exceeded the 1.65% level indicated as the threshold of K deficiency, and frequently exceeded the 2.07% level

Table 49.—Nutrient concentrations in pigeon pee in relation to treatment applied to the Tivivid sand.

pH NPKCl	Ca _n	Nutrients applied, ppm									
		39.25		50.00		100.00		K		150.00	
		100.00	50.00	150.00	39.25	100.00	160.75	50.00	150.00	100.00	160.75
6.35	54.2	--	--	--	--	--	--	--	--	--	--
6.45	80.0	--	1.03	1.05	--	--	--	--	--	--	--
6.80	200.0	1.05	--	--	1.10	1.23	1.23	--	1.10	1.10	1.30
7.15	320.0	--	1.03	0.96	--	--	--	--	1.18	1.13	--
7.45	345.8	--	--	--	--	--	1.15	--	--	--	--
6.35	54.2	--	--	--	--	--	0.29	--	--	--	--
6.45	80.0	--	0.25	0.28	--	--	--	--	0.31	0.29	--
6.80	200.0	0.23	--	--	0.25	0.28	0.28	--	--	--	0.32
7.15	320.0	--	0.23	0.22	--	--	--	--	0.27	0.25	--
7.45	345.8	--	--	--	--	0.25	--	--	--	--	--
6.35	54.2	--	--	--	--	--	--	K	--	--	--
6.45	80.0	--	2.37	2.57	--	--	--	2.50	--	--	--
6.80	200.0	1.98	--	--	2.15	2.32	2.32	--	2.30	2.67	--
7.15	320.0	--	1.80	2.28	--	--	--	2.52	--	2.00	2.32
7.45	345.8	--	--	--	--	--	--	1.82	--	--	--

Table 50.—Nutrient concentrations in pigeon pea in relation to treatment applied to the Kasarama loamy sand.

regarded as adequate (212). The P concentrations were higher by about 100% in plants grown on the Tiwiwid sand than in those grown on the Kasarama soil. The data did not provide any explanation for the necrosis and fall of leaves, and the fact that the soils were fumigated should have minimized the possibility of root pests such as nematodes. There are, however, no actual data on the latter possibility.

Soil Fertility and Amelioration

The patterns of plant growth on the four soils reflected the differences in the properties of the Tiwiwid sand on the one hand and of the three brown sand soils on the other. The strong similarities among the brown sand soils are borne out by the data in Table 51. The means of the levels of dry matter production of pangolagrass and of the levels of nutrient uptake provided by the fitted regression equations, were used to compute the mean levels of concentration. The mean dry matter production ranged from 9.56 g/pot on the Tabela sand to 11.09 g/pot on the Kasarama loamy sand. Mean uptakes of Ca, K, and N were highest from the Kasarama soil, while P uptake followed the soil sequence Tabela > Kasarama > Ebini. The concentration of P in the plants followed the same sequence as P uptake. Among the elements considered, P displayed the greatest variation with soil in terms of both concentration and uptake by the plants. The concentration of N was virtually constant, while concentrations of Mg and K were largest in the plants grown on the Tabela sand, and lowest in those grown on the Kasarama loamy sand.

Table 51. —Mean levels of dry matter yield, nutrient concentrations, and uptake by pangolagrass on the brown sand soils.

Soil	Mean yield g/pot	Mean concentration						Mean uptake mg/pot			
		C _a	Mg	K	N	P	Ca	Mg	K	N	P
Tabela sand	9.56	0.42	0.42	2.05	1.58	0.24	40.43	27.84	195.67	150.63	22.69
Kasarama loamy sand	11.09	0.46	0.25	1.86	1.58	0.19	50.82	27.53	205.75	174.84	20.69
Ebinu sandy loam	10.25	0.42	0.26	1.95	1.55	0.18	42.57	26.49	199.38	159.16	17.92

These differences appeared to be related to the differences in the pH range studied in the different soils and, therefore, in the amounts of the cations which were present in water-soluble forms. The uptake of P may have also been influenced by the differences in pH ranges, but it increased in the same direction as did the proportion of fulvic acids in the organic fraction of the soils, and decreased with increasing amounts of alkali-extractable Al.

Computation of the levels of each of the three nutrients of variable supply in the study, which are required for maximum dry matter production was not conclusive. The data obtained when the partial derivatives of the fitted regression equations were equated to zero and solved, are presented in Table 52. The coded range of nutrient levels was from -1.215 to 1.215, and those extremes were frequently exceeded by the roots of the equations. The computations have no real value, since extrapolation beyond the limits of the experimental area is meaningless (201). They, however, indicate the directions in which treatment levels should be adjusted for the maximization of yields. When decoded, the roots of the equations indicate that dry matter production on the Tabela sand was nearer to a minimum level and that at that point the levels of K and P were 49.5 and 40.5, respectively, and the soil pH somewhat lower than pH 6. Yields on the Ebini sandy loam were also nearer to a minimum than to a maximum. In this soil, excessive levels of K (> 160ppm), and inadequate quantities of P (< 37ppm) combined to produce minimum yields at pH 6.4. The Kasarama loamy sand produced yields which were nearer

Table 52. --Solutions of partial derivatives of fitted regression equations for dry matter yield of pangolagrass.

Soil	Variable					
	Ca		P		K	
	Coded	Uncoded (pH)	Coded	Uncoded (ppm)	Coded	Uncoded (ppm)
Tabela sand	-2.088	<6.0	-0.191	40.5	-1.010	49.5
Kasarama loamy sand	-36.112	<4.9	13.398	>160.0	-15.320	<27.5
Ebinu sandy loam	0.605	6.4	-3.284	<37.0	1.927	>160.0

to the maximum. The conditions for maximum yields on this soil were high P levels ($> 160\text{ppm}$) and low K supplies ($< 37\text{ppm}$) at a pH somewhat less than 4.9. The computations underline the importance of the supply of P to plant growth on these soils; they indicate that relatively small quantities of K are needed and that lower pH levels favor higher yields of pangolagrass.

Growth of pigeon pea and pangolagrass was appreciably better on the Tiwiwid sand. Cation concentrations in the legume were remarkably similar on the Tiwiwid and Kasarama soils, except for Ca concentration which was higher in the plants grown on the Kasarama soil at the lower P levels even though the latter soil had a higher pH level. The better growth of the pigeon pea on the Tiwiwid sand was paralleled by P concentrations which were approximately 100% higher than those obtained on the Kasarama loamy sand.

The shortcomings of the pigeon pea study on the Tiwiwid and Kasarama soils did not permit the effective delineation of differences in response by the two crops to given soil conditions. However, it is not unlikely that the grass would affect the soil differently in terms of its residues, exudates, and relative uptake of nutrients. Differences in the capacities of the plants to modify the rhizosphere are likely to affect the availability of P in the later stages of plant growth and no real meaning can be attributed to the differences in the concentrations of P in the legume as compared to the grass. It is clear, nevertheless, that P added to the brown sand soils did not remain available to plants for long periods of time, nor did its availability improve with time. The Kasarama soil used for the

growth of the pigeon pea plants had previously received 100ppm P, but this treatment did not appear to affect the concentration of P in the plants. Similarly, the Tabela and Ebini soils used for the growth of pangolagrass had been given previous applications of P. The response surface for dry matter yield on the Ebini soil suggested that the P fixation capacity of that soil was at least partly satisfied. Levels of P in the plants were, however, not very different from those on the Kasarama soil which received no previous P treatment.

Practices aimed at the amelioration of the fertility levels of these soils will need to be based on the properties of the soils. Plant growth on the Tiwiwid sand appeared to be limited by the supply of N, while the limiting factor on the three brown sand soils was P. These limitations in the unamended soils were complicated by the inherently low amounts of exchangeable K, Mg and Ca. Though the Tiwiwid sand had a higher base status than the brown sand soils, there was a common factor among the soils in that the source of sites for cation exchange was primarily in the organic fraction. The addition of N, K, Mg, and S is, therefore, likely to be negated by leaching, if the moisture regime of the soils is not controlled. A similar condition applies to P added to the Tiwiwid sand. Each soil derived some benefit from the addition of micronutrients and Ca, but the effect of the latter element on the growth of pangolagrass on the brown sand soils dictates the need for caution in its use.

The yield data for pigeon pea on the Kasarama loamy sand were far from conclusive but indicated a negative effect of increasing pH at low P levels. It is evident that high pH levels depressed dry matter production by pangolagrass. The negative effect of high pH on the brown sand soils was apparently related to decreased P availability to plants. The high correlation between Bray #1 extractable P and plant growth (285) validates the conclusion that only a small fraction of the P added to these soils was available to plants. The effect of increasing pH on the extractability of added P was not clearly demonstrated, but plant uptake of P was obviously lower at higher pH levels.

The negative effect of high pH on the availability of P to plants was contrary to the classically accepted principles of soil fertility, but it has been reported to occur in several tropical and subtropical soils. This effect has been observed on Oxisols in Natal (246), and on several latosols in Hawaii (94). A striking demonstration was provided by an amorphous Entisol from Costa Rica on which a given yield of pangolagrass was attained on the addition of lime, only if amounts of P were applied in proportion to the resulting changes in pH (178). The latosols were generally red-yellow soils and could therefore, be expected to have organic fractions which were dominated by fulvic acids (159, 233, 300). The stability of these acids in the soil depends on their degree of Al saturation (270, 336), and the pH levels of the brown sand soils studied suggest that Al-fulvate complexes may have been the principal agents of buffering. The capacity for competitive binding of fulvates and P by Al has been demonstrated

(163, 168), and the preference for the binding of fulvates at lower pH levels--about 5--can be appreciated by consideration of the pK values of the organic matter (182, 235) and of hydroxy-Al (138). At higher pH levels P is increasingly bonded by Al or Fe at the expense of fulvates, and the addition of P to Al-fulvate soil systems could be expected to result in the formation of more fulvate-Al-P compounds at lower pH levels and the formation of more Al-P at higher pH levels (168). The greater ease of extractability of P from fulvate-(Al, Fe)-P complexes than from Al-P or Fe-P (168), explains at least, in part, the decrease in availability of added P as the soil pH increases. Though both Fe-P and Al-P are known to be capable of supplying P to plants (7, 118, 178, 294, 331), it is also known that Al and Fe compounds are least soluble at pH 6 to 8 (238). Further, though Al-P tends to become the more important form of P as the soil pH increases (118, 178), the solubility of Al-P is depressed by Ca (328).

In addition to their role in P retention, the hydrous oxides influence the relative amounts of exchangeable cations in the soil. The oxides favor the retention of Ca (134), but render K more soluble (187, 193, 297). The low amounts of exchangeable K in the soils relative to the total soil contents of K and uptake of K by pangolagrass were probably indicative of the operation of a K equilibrium condition, which is controlled by amorphous Al-and Fe-silicates (222, 304). The increase in exchangeable Ca in the brown sand soils on addition of P was likely to be due to the sorption of

P by hydroxy-Al and hydroxy-Fe, with an increase in the negative charge on the surface of the sesquioxide (24, 123).

The sources of acidity-- H^+ and ionic Al--are both likely to be neutralized at or below pH 5.4 (16, 274, 341). Maximum yields of pangolagrass on the brown sand soils are to be expected at pH < 5.4. This, taken in conjunction with the adverse effects of high pH on the retention of K and Mg, and on the availability of P, as well as the low Ca uptake by the grass, suggested that exchangeable Al is likely to be the most meaningful criterion for liming practices on these soils. The replacement of organic matter by OH^- in organic matter sesquioxide complexes at higher pH levels (168) is likely to be conducive to the loss of organic matter by leaching with subsequent structural deterioration, and this makes an additional argument against the use of large amounts of lime.

The differences in fertility between the Tiwiwid and the brown sand soils seem to hinge on the proportions of sesquioxides present. These differences are manifest largely in the availability of added P, and the optimum pH levels of the soils. The amelioration of the fertility levels of the soils should have as its immediate objective the increase of the capacities of the soils to retain nutrients against percolating water and the provision of adequate levels of available P. The low levels of pH which have been shown to be desirable in the brown sand soils, suggest that the amelioration of fertility levels can be achieved by the judicious exploitation of the effects of additions of P to these soils. These effects of P addition which serve to increase K retention (15), pH and CEC (232), N fixation

(81) and promote the accumulation of organic matter (262, 329) suggest that the quenching of the P fixation capacity of the soils should be attempted with close attention being paid to any ecological changes that may occur (219). The source of P likely to be most satisfactory in this context appears to be superphosphate.

SUMMARY AND CONCLUSIONS

The soils of the "white sand" plateau of Guyana are all highly weathered, having developed from materials eluviated from the weathered surfaces of the Guiana Shield, and deposited in their present positions during the third interglacial period.

Laboratory studies revealed that the Tiwiwid sand and three brown sand soils were comprised largely of quartz, and that their contents of clay in the surface horizons increased in the order: Tiwiwid < Tabela < Kasarama < Ebini. This sequence is the reverse of the elevation of the soils. The clay contents also increased with depth in the profile in the Tabela, Kasarama, and Ebini soils. The clay fraction of the soils consisted largely of poorly crystalline kaolinite, and had < 10% of its weight in the form of sesquioxides. Gibbsite was absent from each of the soils. The sesquioxides were amorphous and associated with substantial quantities of SiO_2 . Hydrous Al apparently originated from the degradation of kaolinite crystals, and was retained in the Tabela, Kasarama, and Ebini soils through its interaction with the organic fraction. The sesquioxide content of the Tiwiwid sand was very much lower than that of the three brown sand soils, and most of the hydrous Al was present in an exchangeable form.

The soils were very poorly supplied with plant nutrients, and though the total contents of the major nutrient cations were

unexpectedly high, very small proportions of these were in exchangeable forms. The soils can be put into groups on the basis of their level of exchangeable nutrients and sesquioxides. The Tiwiwid sand with its high nutrient supply and lower sesquioxide content constitutes one group while the Tabela, Kasarama, and Ebini soils comprise the other group. The soils of the latter group were also different from the Tiwiwid sand in that their organic fractions were dominated by fulvic acids rather than humic acids, and their pH levels in the natural state suggested that Al-fulvate complexes provided the main source of buffering. The Tiwiwid sand had a substantial portion of its P content in easily extractable forms, while the brown sand soils had < 2ppm P extractable by the Bray #1 solution.

A common characteristic among the soils was the source of the soil CEC. More than 90% of the CEC in each of the soils was contributed by the organic fraction, almost exclusively by the humic acids. This entailed a similarity in the pattern of retention of cations in the soils, such that Ca was preferentially bonded, while K and Mg tended to remain in solution. Thus, the ease of loss of nutrients by leaching was a property of the soils derived from the essentially organic nature of the exchange complex. Modification of the pH of the soils by the application of lime decreased the amounts of K and Mg retained in exchangeable form, while the addition of P seemed to increase the amounts of exchangeable Ca. Added P remained almost completely extractable from the Tiwiwid sand, but < 70% was recoverable from the brown sand soils. In the brown sand soils it seemed that

P was adsorbed on Al-fulvate complexes, possibly displacing fulvates at higher levels of addition. Increasing soil pH enhanced the replacement of fulvate by OH⁻ and/or P, and increased the amounts of P fixed by the soils.

Plant growth on the soils reflected the broad division of the soils into the groups. Higher yields were produced on the Tiwiwid sand with higher plant P concentration, and the nutrient most likely to limit growth on this soil seemed to be N. On the brown sand soils, plant growth responded markedly to additions of P. Micronutrients were also in limited supply, but it will be necessary to study the effects of the individual micronutrients. Nodulation of pigeon pea was greatly improved by the addition of P and micronutrients to the soils. Both the size of the nodules and the development of hemoglobin within them were improved by the addition of these nutrients. Positive responses to lime are to be expected on the Tiwiwid sand, but on the brown sand soils, higher yields are more likely at lower pH levels. This is particularly true of pangolagrass. On the latter soils, P fixation restricted plant growth even though the plants developed very healthy appearances. The optimum pH level for maximum yields is likely to vary with the type of crop, and with its modification of the conditions in the rhizosphere.

Improvement of the fertility levels of the brown sand soils must achieve an increase in the capacity of the soils to retain cationic nutrients against leaching and to supply adequate levels of P. This will probably be best effected by the use of P fertilizers,

e.g., superphosphate, which ultimately will satisfy the P fixation capacities of the soils, and promote the build up of organic matter. The new store of organic matter is likely to be less fulvate in character, and cultural practices must be designed to accomodate such changes. The use of lime will need to be carefully controlled in order to minimize the possibilities of the soils becoming entirely inorganic in composition.

The following conclusions appear to be justified from the results of this study:

- (a) Kaolinite, the only clay mineral present in these soils exhibited various degrees of degradation and made little or no contribution to the chemical properties of the soils.
- (b) The absence of gibbsite and the physical condition of the clay crystals suggested that much of the amorphous Al in the soils may have been derived from the destruction of the clay crystals.
- (c) The organic fractions of the soils varied in chemical composition, with those of the three brown sand soils being predominantly fulvic in character, and that of the Tiwiwid, predominantly humic.
- (d) Complexes of organic matter and Al, principally Al-fulvates, appeared to provide the buffering mechanism of the brown sand soils, while the Tiwiwid soil seemed to be buffered by the organic matter, per se.
- (e) The nutrient status of each of the soils was very low, and mineral sources of nutrients were virtually absent.

(f) The CEC of the soils was due to the organic fraction, apparently to the humic acids in particular. The exchangeable cations constituted a very small portion of the total amounts of cations in the soil, probably because of the penetration of the cations into the gel-like organic matter.

(g) The organic nature of the cation exchange sites favored the preferential bonding of Ca and the exclusion to a great degree of K and Mg. This effect was more marked at higher pH levels, and increased the possibility of loss of K and Mg by leaching.

(h) The addition of P increased the CEC of the soils. Virtually all of the P added to the Tiwiwid soil was extractable, but very little of that added to the brown sand soils.

(i) Plant growth was much better on the Tiwiwid sand than on the brown sand soils at comparable nutrient levels when the moisture regime was controlled.

(j) The improvement of fertility levels of the Tiwiwid sand can be effected by increasing the pH of the soil, and supplying adequate levels of all nutrients in plant available, but not readily leachable, forms.

(k) The fertility levels of the brown sand soils can be improved by the addition of adequate levels of all nutrients as in the Tiwiwid sand, but the pH levels of the soils need to be carefully controlled in relation to the crop to be grown and the capacity of the soils to fix P.

(l) The use of P as the principal agent of improvement of the

chemical properties of the brown sand soils seems to hold the most promise of prolonged utilization.

(m) Commercial utilization of the brown sand soils will depend almost entirely on the technology available in relation to soil conservation and moisture control.

APPENDIX

Table 53. --Shoot weights (oven-dried) from first harvest of pangolagrass.

Treatment	Soil			
	Tiwiwid	Tabela	Kasarama	Ebjini
	g/pot			
Control	6.0	0.3	1.6	1.8
N	5.3	0.9	0.8	1.6
S	7.6	0.2	0.5	1.0
P	7.6	1.2	5.7	3.0
K	4.7	0.3	1.1	0.9
Tr	6.8	0.3	0.3	0.6
NS	3.6	1.0	1.7	2.3
NP	9.7	4.2	6.1	4.5
NK	9.3	0.6	1.1	1.8
NTr	10.5	0.2	0.6	0.3
SP	4.1	4.5	4.8	5.2
SK	6.9	0.9	2.0	1.0
STr	10.5	0.6	0.9	1.1
PK	6.6	0.8	5.3	4.3
PTr	8.7	4.5	6.0	3.8
KTr	0.6	0.5	0.8	2.7
NSP	7.7	4.9	7.6	3.0
NSK	7.2	0.9	1.9	3.0
NSTr	9.6	0.5	1.1	0.8
NPK	13.7	7.5	8.1	6.6
NPTr	5.3	4.6	4.4	1.3
NKTr	13.0	0.3	1.2	0.3
SPK	4.9	3.6	5.1	5.1
SPTr	10.1	5.2	5.5	3.7
SKTr	9.1	0.5	0.5	0.2
FKTr	6.1	4.9	5.0	1.2
NSPK	3.1	10.0	9.8	8.0
NSPTr	9.9	3.6	8.1	5.2
NSKTr	6.1	0.6	3.0	0.2
NFKTr	1.8	6.5	12.6	6.9
SPKTr	10.2	5.3	7.2	3.1
NSFKTr	8.9	3.3	10.1	1.2

Table 54. --Shoot weights (oven-dried) from second harvest of pangolagrass.

Treatment	Soil			
	Tikiwid	Tabela	Kasarawa	Ebini
	g/pot			
Control	2.8	0.2	2.7	2.6
N	8.3	0.6	0.2	2.6
S	4.3	1.1	0.1	1.0
P	4.9	4.0	4.0	4.3
K	5.5	0.2	1.1	0.9
Tr	3.9	0.2	0.4	2.3
NS	1.6	0.2	2.0	2.1
NP	6.3	3.6	2.4	4.2
NK	8.0	0.2	0.9	1.4
NTr	5.4	0.2	0.2	0.6
SP	5.3	2.7	3.3	3.5
SK	5.9	0.5	0.5	0.9
STr	4.1	0.3	0.6	2.8
FK	5.0	1.0	5.0	3.2
PTr	3.1	2.9	4.1	3.4
KTr	3.8	0.2	0.3	1.2
NSP	7.6	2.5	2.9	8.0
NSK	8.2	0.7	4.2	3.9
NSTr	5.1	0.5	0.7	0.9
NPK	10.8	10.0	10.0	11.1
NPTr	11.8	3.1	3.5	0.9
NKTr	8.7	0.2	0.5	1.3
SPK	4.7	3.9	2.5	3.6
SPTr	5.0	3.2	3.7	4.6
SKTr	4.1	0.2	0.1	0.1
FKTr	5.2	2.7	4.0	3.9
NSPK	0.9	6.3	6.8	8.3
NSPTr	8.3	3.0	4.8	6.1
NSKTr	0.3	1.0	0.9	2.8
NPKTr	16.4	12.1	3.8	10.5
SPKTr	3.0	4.6	3.9	3.5
NSFKTr	13.6	13.1	6.1	2.9

Table 55. —Analysis of variance for data shown in Table 24.

Soil	Source	d.f.	M.S.	F	
				F	F
Tiwivid sand	N	1	25.6865	5.83*	
	S	1	8.0300	1.82	
	P	1	4.9063	1.13	
	K	1	1.4578	0.33	
	Tr	1	11.4840	2.61	
Error	26		4.4084		
Total	31				
Tabela sand	N	1	16.8200	7.20*	
	S	1	0.6903	0.30	
	P	1	147.0613	62.91**	
	K	1	10.9278	4.68*	
	Tr	1	0.5513	0.24	
Error	26		2.3376		
Total	31				
Kasarama loamy sand	N	1	12.8145	9.89*	
	S	1	0.5126	0.40	
	P	1	168.1320	129.72**	
	K	1	9.6251	7.43*	
	Tr	1	0.4876	0.38	
Error	26		1.2961		
Total	31				

Table 55. --Continued.

Soil	Source	d.f.*	M.S.	F
Ebuni sandy loam	N	1	9.0845	2.54
	P	1	0.0751	0.03
	K	1	99.8592	31.11**
	S	1	2.2313	0.87
	Tr	1	9.1913	3.58
Error		26	2.5672	
Total		31		

** Significant at the 0.01 probability level.

* " " 0.05 " "

Table 56. --Analysis of variance for data shown in Table 27.

Soil	Source	d.f.	M.S.	F
Tiwiwid sand	N	1	4.7278	5.32*
	S	1	1.3203	1.49
	P	1	1.2403	1.40
	K	1	3.8593	4.23
	Tr	1	6.3903	7.19*
	Error	26	0.8891	
	Total	31		
Tabelia sand	N	1	4.5753	12.18**
	S	1	0.0153	0.04
	P	1	91.1628	243.51**
	K	1	0.0003	0.00
	Tr	1	2.5778	9.53**
	Error	26	0.3726	
	Total	31		
Kasarama loamy sand	N	1	4.2513	6.32*
	S	1	0.3200	0.46
	P	1	61.6050	89.41**
	K	1	0.5770	0.73
	Tr	1	2.61	3.84
	Error	26	0.6801	
	Total	31		

** Significant at the 0.01 probability level.

* " " " " 0.05 " "

Table 57. -Analysis of variance for data shown in Table 29.

Soil	Source	d.f.	M.S.	F
Tiwiwid sand	N	1	2.3113	1.16
	S	1	5.7800	2.99
	P	1	0.3200	0.16
	K	1	13.2600	6.65*
	Tr	1	2.6450	1.33
	Error	26	1.3928	
	Total	31		
Tabela sand	N	1	0.2278	0.47
	S	1	0.0153	0.03
	P	1	24.6753	107.05**
	K	1	0.0528	0.11
	Tr	1	1.3203	5.72*
	Error	26	0.2205	
	Total	31		
Kasarama loamy sand	N	1	0.0153	0.09
	S	1	0.0078	0.05
	P	1	12.3753	77.00**
	K	1	0.0578	0.24
	Tr	1	0.0028	5.26*
	Error	26	0.1607	
	Total	31		

** Significant at the 0.01 probability level.

* Significant at the 0.05 probability level.

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He worked in the Extension Service of the Ministry of Agriculture, British Guiana, from July, 1961, to December, 1965, and then with the Research Division of the Ministry. He enrolled at Tuskegee Institute, Alabama, in February, 1967, and completed the degree of Master of Science under the guidance of Dr. K. S. Chahal in August, 1968. He came to the University of Florida in September, 1968, with the award of a graduate assistantship from the Center for Tropical Agriculture and the Department of Soils, and since then has worked toward the degree of Doctor of Philosophy in Soil Science.

Alfred Victor Downer is married to the former Loretta F. Henry, and is the father of three children. He is an associate member of Sigma Xi honor society, and a member of the Soil Science Society of America, the American Society of Agronomy, and the American Institute of Biological Sciences.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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