

CHEMISTRY AND NUTRIENT ELEMENT STATUS  
OF SELECTED LIBERIAN SOILS

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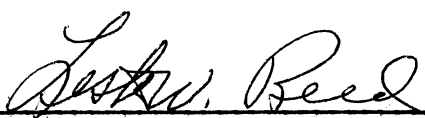
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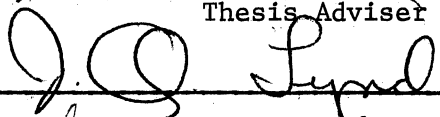
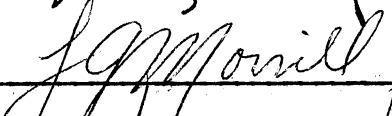
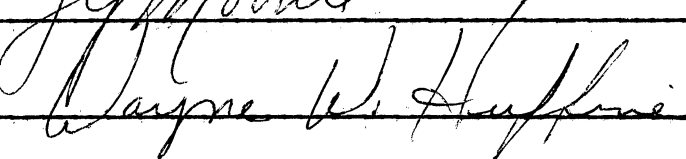
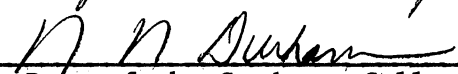
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## TABLE OF CONTENTS

Chapter	Page
I. INTRODUCTION . . . . .	1
II. REVIEW OF LITERATURE . . . . .	4
Particle Size Distribution . . . . .	8
Cation Exchange Capacity and Exchange Cations in Soils. . . . .	9
Availability and Nutrient Requirement of Plants . . . . .	13
Exchange Acidity . . . . .	17
Phosphorus. . . . .	21
Organic Matter and Nitrogen. . . . .	32
Clay Minerals. . . . .	39
III. MATERIALS AND METHODS. . . . .	44
IV. RESULTS AND DISCUSSION . . . . .	50
Particle Size Distribution. . . . .	50
Chemical Properties of the Soils. . . . .	56
Nutrient Element Requirements . . . . .	70
Mineralogical Properties. . . . .	88
V. SUMMARY AND CONCLUSION . . . . .	110
LITERATURE CITED. . . . .	115
APPENDIX . . . . .	123

## LIST OF TABLES

Table	Page
I. Baker's Solution No. 6 M X 10 <sup>4</sup> . . . . .	47
II. Particle Size Distribution: Comasadu I and Dalin II Samples Used in Mineral Analysis . . . . .	51
III. Particle Size Distribution: Foya Model III Soil Samples Used in Mineral Analysis . . . . .	51
IV. Particle Size Distribution: Foya Deep IV Soil Samples Used in Mineral Analysis . . . . .	52
V. Particle Size Distribution: Makona V Soil Samples Used in Mineral Analysis . . . . .	52
VI. Particle Size Distribution: Konjo VI Soil Samples Used in Mineral Analysis . . . . .	53
VII. Particle Size Distribution: N'gisi Konja VII Soil Sample Used in Mineral Analysis. . . . .	53
VIII. Particle Size Distribution: Red Weledu VIII Soil Samples Used in Mineral Analysis . . . . .	54
IX. Particle Size Distribution: Red Weledu/Stones IX Soil Samples Used in Mineral Analysis . . . . .	54
X. Particle Size Distribution: Yellow Weledu X Soil Samples Used in Mineral Analysis . . . . .	55
XI. Chemical Characteristics of the Comasadu I Soil. . . . .	57
XII. Chemical Characteristics of the Dalin II and Foya Model III Soils. . . . .	58
XIII. Chemical Characteristics of the Foya Deep IV Soil. . . . .	59
XIV. Chemical Characteristics of the Makona V Soil. . . . .	60
XV. Chemical Characteristics of the Konjo VI Soil. . . . .	61
XVI. Chemical Characteristics of the N'gisi Konja VII Soil. . . . .	62
XVII. Chemical Characteristics of the Red Weledu VIII Soil. . . . .	63

Table	Page
XVIII. Chemical Characteristics of the Red Weledu/Stones IX Soil . . . . .	64
XIX. Chemical Characteristics of the Yellow Weledu X Soil. . . . .	65
XX. Mean Average Chemical Characteristics of Each Series of Soil (I-X) . . . . .	66
XXI. Soil Characteristics of Nutrient Elements Requirements (Baker's Procedure) . . . . .	71
XXII. Correlation Coefficients Due to Soil Factor: Total Phosphorus (PPM) Versus Other Fractions . . . . .	74
XXIII. Correlation Coefficients Due to Soil Factors: Available P (PPM) Versus Other Fractions. . . . .	75
XXIV. Correlation Coefficients Due to Soil Factors: Organic Matter Versus Other Fractions . . . . .	76
XXV. Correlation Coefficients Due to Soil Factors: Organic P (PPM) Versus Other Fractions. . . . .	77
XXVI. Other Correlation Coefficients that are Due to Soil Factors and are Significant . . . . .	78
XXVII. Significant Correlation Coefficients: Soil Effects Removed Total Phosphorus Versus Other Fractions . . . . .	79
XXVIII. Significant Correlation Coefficients: Soil Effects Removed Available Phosphorus (PPM) Versus Other Fractions . . . . .	80
XXIX. Organic Phosphorus (PPM) Versus Other Fractions . . . . .	81
XXX. Significant Correlation Coefficients: Soil Effects Removed Baker's Calcium Versus Other Fractions. . . . .	82
XXXI. Baker's Magnesium Versus Other Fractions. . . . .	82
XXXII. Baker's Potassium Versus Other Fractions. . . . .	83
XXXIII. Significant Correlation Coefficients: Soil Effects Removed Organic Matter Versus Other Fractions . . . . .	83
XXXIV. % Total Nitrogen Versus Other Fractions . . . . .	84
XXXV. Significant Correlation Coefficients: Soil Effects Removed Exchangeable Calcium Versus Other Fractions . . . . .	84

Table	Page
XXXVI. Exchangeable Magnesium Versus Other Fractions . . . . .	85
XXXVII. Exchangeable Potassium Versus Other Fractions . . . . .	85



## LIST OF FIGURES

Figure	Page
1. X-ray Diffractograms for the Comasadu I Soil: (1) Ca-Saturated, (2) K-Saturated (Air-Dried), (3) K-Saturated and Heated to 500°C. Measurements in Angstroms. . . . .	89
2. X-ray Diffractograms for the Foya Model III Soil Measured in Angstroms. (1) Ca-Saturated, (2) K-Saturated (Air-Dried), and (3) K-Saturated and Heated to 500°C. . . . .	91
3. X-ray Diffractograms for the Foya Deep IV Soils Measured in Angstroms. (1) Ca-Saturated, (2) K-Saturated (Air-Dried), and (3) K-Saturated and Heated to 500°C. . . . .	93
4. X-ray Diffractograms for the Foya Deep IV Soil Measured in Angstroms. (1) Ca-Saturated, (2) K-Saturated, and (3) K-Saturated and Heated to 500°C . . . . .	94
5. X-ray Diffractogram for the Makona V Soil Measured in Angstroms. (1) Ca-Saturated, (2) K-Saturated (Air-Dried), and (3) K-Saturated and Heated to 500°C. . . . .	96
6. X-ray Diffractograms for the Makona V Deep Subsurface and the Dalin II Surface Soil Measured in Angstroms. (1) Ca-Saturated, (2) K-Saturated (Air-Dried), and (3) K-Saturated and Heated to 500°C. . . . .	97
7. X-ray Diffractograms for the Kanjo VI Soil Measured in Angstroms. (1) Ca-Saturated, (2) K-Saturated (Air-Dried), and (3) K-Saturated and Heated to 500°C. . . . .	101
8. X-ray Diffractograms for the N'gisi Konja VII Soil Measured in Angstroms. (1) Ca-Saturated, (2) K-Saturated (Air-Dried), and (3) K-Saturated and Heated to 500°C. . . . .	102
9. X-ray Diffractograms for the Red Weledu (Foya) VIII Soil Measured in Angstroms. (1) Ca-Saturated, (2) K-Saturated (Air-Dried), and (3) K-Saturated and Heated to 500°C . . . .	104
10. X-ray Diffractograms for the Red Weledu (Stones) IX Soil Measured in Angstroms. (1) Ca-Saturated, (2) K-Saturated (Air-Dried), (3) K-Saturated and Heated to 500°C . . . . .	106

11. X-ray Diffractograms for the Yellow Weledu X Soil Measured in Angstroms. (1) Ca-Saturated, (2) K-Saturated (Air-Dried), and (3) K-Saturated and Heated to 500°C . . . . . 108

## CHAPTER I

### INTRODUCTION

Liberia is on the West Coast of Africa bounded by Sierra Leone in the northwest, Guinea in the north, Ivory Coast in the East and the Atlantic ocean on the south.

The climate is tropical (warm - humid) with marked wet and dry periods. Annual rainfall along the coast averages about 205 in. (521 cm.), decreasing southeastward to 100 in. (254 cm.), and diminishing inland to about 70 in. (170 cm). Seventy-five to 88 percent of the rain normally falls between May and October. The daily minimum temperature along the coast averages 72-74<sup>o</sup>F and the maximum temperature averages 80-87<sup>o</sup>F.

The land along the coast is flat and sandy with many long narrow lagoons. The land rises from the coast to small hills and mountains. The inland geology is a type of Precambian metamorphic rock which has given rise to red acidic soils. The flora is essentially tropical rain forest excepting the north, northwest and coastline which is savannah-like.

Reed (81) has classified the vegetation of the land into four different belts:

- (1) Coastal forest and mangrove swamps occurring in narrow strips from 1 to more than 9 miles in width running parallel with the seacoast.

- (2) Evergreen rain forest that begins on the highlands near the sea coast and extends inland about 30 miles in the rainfall belts of 100 - 200 in. (254-508 cm). per year.
- (3) Deciduous forest that begins 40 to 50 miles inland along a line roughly parallel to the sea coast,
- (4) Savannah and dark forest vegetation occurring in the extreme northern portion of the western part of the country.

The country is economically dependent upon the slash and burn traditional farming system with approximately 90-95 percent of the population engaged in agriculture. The traditional farming system, involves cutting down the bush, burning it, and clearing the land for cultivation. The farm family moves to a new tract for each crop season.

Reed (81), who was the first to do any scientific soil research in Liberia has reported that this burning enriches the nutrient status of the soil. This claim has also been supported by Baldanzi (9).

Export products are iron ore, rubber, timber, coffee, cocoa, piassava, and palm kernel. Rice is a major food crop in Liberia. Its cultivation occupies most of the working hours of the farmer. But the yield of rice is low and inadequate for domestic purposes thus it is not an export crop. Additional rice is imported for domestic consumption.

The introduction of concession companies and ancillary enterprises have had some marked effects on the Liberian economy and domestic food production. These new sources of employment draw labor out of the traditional farming economy. Therefore, the ability of agriculture to carry on its task of feeding the population has declined. With a

traditional agricultural economy, the mobility of labor from the agricultural sector can bring about an adverse situation. This labor mobility makes it mandatory to shift the agricultural system from one dependent on a large volume of manual labor to one which can successfully cope with problems of labor scarcity. This problem requires a wise and intensive use of all available resources.

This study is an attempt to examine one of the most important resources (soil) of the country. Up to the present time very little information concerning Liberian soils and their physical and chemical properties have been gathered. Except for Reed's (81) reconnaissance soil survey work and fertilizer trials on small plots, not true scientific and continuous soil investigations have been attempted on Liberian soils. This study is an investigation of some of the chemical characteristics of Liberian soils and the concentration of major nutrient elements, base status, soil reaction, organic matter, and nutrient element availability for plants. The mineralogy of these soils and its effect on the soil properties was also investigated. It is also the objective of this research to increase our understanding of how to begin a study of soil management and crop production.

## CHAPTER II

### REVIEW OF LITERATURE

In 1944 Reed (81) took the first step in a pioneering investigation to obtain information on the soils of Liberia. Since the report by Reed was published, there has been no significant soil research undertaken except for a few fertilizer trials.

Reed (81) classified the soils of Liberia as Latosols for 75 percent of the total area of the country, Lithisols 16.7% percent, and Regosols 2.5 percent. Other small groups of soils are: alluvial soils 2.5 percent, mangrove swamp soils 0.8 percent, half-bog soils 0.4 percent and Gray Hydromorphic soils 2.5 percent.

Most of the upland soils are yellow-brown latosols (probably equivalent in character to oxysols) with distinct Bt horizons, but becoming more red (character Ochrasols) towards the drier section of the country (north) (104). They are usually rich in ironstone gravel even under high forest. Worrall and his coworkers (104) claimed that the red loamy soils (character Basisols) developed over numerous basaltic dikes along the coast. The parent materials of these soils are crystalline metamorphic and igneous rocks.

According to Reed (81) the organic matter content of the latosols under virgin forest averages about 6 percent in the surface 6 inches of soil and 2.5 percent at depth of 3-6 inches. For soils under a secondary growth, the organic matter averages 4 percent and 2 percent

respectively. This information reveals that the soils used for "shifting farming" contain about 25 percent less organic matter than they initially contained.

The nitrogen content of these latosols is said to correlate closely with the amount of organic matter present (79). The soil organic matter-nitrogen ratio averages about 30 and the carbon-nitrogen ratio about 17 (81). The soluble phosphorus content varies from 4 ppm to 15 ppm. It averages about 8 ppm in the top soil and about 5 ppm in the subsoil. These latosols are strongly acid in the subsurface where the pH averages 4.50. The extremely acid subsoil has a pH average of 3.85 (81).

The average cation exchange capacity for soils under virgin forest is about 12, and 9 for those under secondary fallow. The difference is attributed to the high organic matter content of the virgin forest soils. At the 3-6 inch depth, the cation exchange capacity averages about 8 and below 3-6 inches about 5. According to Reed (81) burning of the bush before cultivation increases the nutrient status of the soil while it decreases the soil acidity. He found that on recently burnt land the soluble-phosphorus content of the surface 3 inches increases from 8 ppm to 18 ppm and base saturation increased from 30 to 46 percent and acidity decreased from pH 4.6 to 5.3.

The lithosols developed on hilly and steeply sloping land are shallow soils (81). Most of the deeper soils in these areas are due to colluvial deposits at the bottom of the slopes. The vegetation consists mainly of trees and shrubs. The structural pattern of the soil often appears to retain the properties of the parent material, "rotten rock". The clays in some of these lithosols are plastic while others

exhibit non-plasticity (81). The surface three inches is described as having 5 percent organic matter, 13 ppm soluble phosphorus, an average pH of 4.4, and a cation exchange capacity of 12. The subsurface 3-6 inch layer has a CEC of 6 and an average pH of 3.9 with about 2.3 percent organic matter. The extreme topographic variation of the lithosols and their shallowness causes them to be of limited agricultural value.

The Regosol group of soils consists of sandy soils and they occur in narrow belts along the coast and in several small tracts inland. The vegetation consists of a sparse stand of savannah grass and palms. Worrall et al. (104) reported that analytical work by Van Boren indicates that the soils of Liberia are non-marine in origin and the parent rock is primarily pre-cambrian metamorphic rocks.

More work has been reported on fertilizer trials than on soils. Most of the experiments however, were carried out with commercial mixed fertilizers (15-15-15) or (10-10-10).

Worrall et al. (104) reported that the most sustained work in fertilizer trials has been on rubber at Harbel (Firestone Rubber Plantations Company) and on rice. As reported by these investigators, McIndoe who worked with fertilizers on rubber plantations for several years reached the following conclusions in 1952:

- (1) N + P on mature trees depressed the yield;
- (2) P alone increased growth but not yield;
- (3) N is necessary for latex in mature trees;
- (4) K is beneficial but the amount required is not certain; and
- (5) K + N gives definite increases in yield.

In 1957, copper deficiency was confirmed and considered the cause



of the inefficient use of the major nutrient elements by rubber trees (104).

Fertilizer trials with rice showed that all treatments except nitrogen alone and potassium alone were beneficial. It was recommended that a fertilizer rate in excess of 60-60-60 per acre would be most profitable.

According to several soil scientists (15,18,65) the soils of Liberia can be placed in the ultisol order. Red-yellow podzolic soils are presently recognized as Ultisols. Extensive leaching is prerequisite to the formation of these soils (18). The mean annual soil temperature is greater than  $23^{\circ}\text{C}$  ( $74^{\circ}\text{F}$ ) a diagnostic criterion for the Ultisol order (18). Characteristics of these soils is a clay mineral suite that is stable under the ambient environment. The suite is dominated by kaolinite, associated with gibbsite and chlorite-vermiculite intergradational calys (18). According to Russell (83) these kaolinites are probably present as halloysites; free silica recrystallizes as quartz, opal, or chalcedony; the aluminum is present as gibbsite or hydrargillite and the iron as limonite  $\text{FeO}(\text{OH})$  and hematite ( $\text{Fe}_2\text{O}_3$ ). Lessivage, leading to the formation of albic and argillic horizons is pronounced. Some of the clay accumulation in the argillic horizon is in the form of argillians (18). Podzolization also occurs in these profiles. The albic horizon is low in free iron oxide but the argillic horizon is rich (18).

According to Bennema (15) the latosols are the most extensive of the red and yellow soils of the tropics and subtropics. The constitution of the mineral soil mass of these soils consists of sesquioxides; 1:1 lattice clay minerals, quartz and other minerals

## Particle Size Distribution

Particle size distribution is one of the most stable soil characteristics. Interest in particle size distribution centers around its use as a basis for soil textural classification (16). It is a valuable information in solving problems dealing with weathering, segregation of soil particles by leaching, soil structure, and sediment transport by water and wind (16). The determination of particle size distribution was originally called "mechanical analysis" but today it is referred to as "particle-size analysis" (16).

Jennings, Thomas, and Gardner (49) in 1922 recommended the use of pipette for particle size analysis of soils. Their method consisted of shaking a dilute, fully dispersed soil suspension in a cylindrical vessel, placing it in an upright position, and determining the concentration of the suspension with the time at measured distances below the surface. The procedure assumes that the particles fall as individuals at a constant rate, irrespective of the presence of other particles. It classifies the soil separates into fractions according to their rate of fall.

In 1926 Bouyoucos (19) devised the hydrometer method which could be used to determine the amount of the various soil particle sizes in a soil suspension. Using the Zuevnes Lactodensimeter with a thermometer in its stem, he could measure the density of suspension of a soil after different periods of settling.

The hydrometer became quite useful in this area of soil analysis. However, it had some major limitations which affected test results. According to Day (31) the hydrometer failed to fulfill the Stoke's equation which is given by the formula: 
$$V = \frac{2}{9} \frac{(d_p - d)gr^2}{n}$$
 where

$V$  = velocity of fall in centimeter per second,  
 $g$  = acceleration due to gravity,  
 $\rho_p$  = density of the particle,  
 $\rho_l$  = density of the liquid  
 $r$  = radius of the particle in centimeters, and  
 $\eta$  = the absolute viscosity of the liquid.

In 1950, Day (31) reported a new method of calibration of the hydrometer for determining particle size. He found that in a particular soil suspension settling under gravity, the concentration of the suspended soil at an arbitrary time after mixing to be a logarithmic function of depth. He based his method on the hypothesis that a logarithmic concentration gradient might be a general characteristic of soil suspensions undergoing sedimentation.

In 1951, Bouyoucos (20) recalibrated the hydrometer to conform with the present soil particle size classification of the USDA and of the International Society of Soil Science.

#### Cation Exchange Capacity and Exchange Cations in Soils

In 1850, Thompson, as reported by Kelley (54), set out to investigate the absorption process by soil. His first attempt dealt with (1) whether ammonia, when absorbed by soil could be leached out by rain water, (2) whether soils differ one from another in their ammonia absorbing-powers, and (3) whether ammonium-sulfate was absorbed.

He added to a soil 0.64 grams of  $(\text{NH}_4)_2\text{SO}_4$  or  $(\text{NH}_4)_2\text{CO}_3$  in solution and he discovered that a greater part of the  $(\text{NH}_4)_2\text{SO}_4$  converted into  $\text{CaSO}_4$ . He concluded that  $\text{NH}_4$ -adsorption was associated

with lime in the soil. He recovered only one-fourth of the added  $(\text{NH}_4)_2\text{SO}_4$  and one-eighth of the  $(\text{NH}_4)_2\text{CO}_3$ .

He then percolated soil columns with similar solutions of  $(\text{NH}_4)_2\text{SO}_4$  and  $(\text{NH}_4)_2\text{CO}_3$  and observed that the  $\text{NH}_4$  in both solutions was absorbed by the soil. He later leached a soil column with a  $\text{NaCl}$  solution and based on his chloride determination, erroneously concluded that sodium is not absorbed by the soil.

Thompson was later supported by Way who also found that  $\text{NH}_4$  could be absorbed by complex double silicates of aluminum and sodium. In an experiment it was observed that the reaction of the aluminosilicates with solutions of  $\text{NH}_4\text{Cl}$  or  $(\text{NH}_4)_2\text{SO}_4$  resulted in the replacement of Ca, Na, or K with the formation of  $\text{NH}_4$  aluminosilicates (54). Way held that the replacement process was irreversible and he was supported by Liebig (54).

Frank according to Kelley (54) was one of the pioneering soil scientists to demonstrate displacement phenomenon in a soil column. He noted that the concentration of a leachate decreases progressively with depth of the column and that addition of  $\text{NaCl}$  to a  $\text{KCl}$  solution reduces the absorption of K from that solution.

The cation exchange capacity phenomenon, which was initiated by Thompson, came to occupy a greater portion of the literature in the middle and late 1800's. Research in this area expanded quite rapidly during the early 1900's.

Mattson (62) explained that cation exchange capacity is a function of pH. At a given pH, the exchange capacity is a definite quantity for a sample, but different from that at another pH.

By microscopical, chemical, and x-ray examination, soil scientists

(43,55) found that the very fine soil fraction contained crystalline substances and that a sample may give characteristic x-ray diffraction patterns that can be said to arise from one of the clay minerals.

Both Albrecht (3) and Grimm (40) pointed out that the exchange properties of soil is largely due to the clay minerals. Bean (13) indicated that the clay fraction ( 2 ) and the organic matter of the soil are responsible for ion exchange. The work of Marshall and Patnaik (60) also corroborates other investigations.

Russell (83) showed that exchangeable cations in a soil can be displaced by washing the soil with a salt solution that contains a cation uncommon to the soils or by washing with a dilute acid. The ions in the extract are part of the readily available elements required by plants. He refers to the uptake of ions by plants and their release by the plant roots as the exchange process in soil.

Jackson (47) defines the cation exchange capacity as arising from proximity to surfaces of negative charges on minerals and organic solids. In many polysilicate clays,  $Al^{+3}$  substitutes for  $Si^{+4}$  in the tetrahedral sheet or  $Mg^{+2}$  for  $Al^{+3}$  in the octahedral sheet, for example, in micas, vermiculites and smectites. A second source of negative charge is broken bonds at crystal edges.

Negative charge must occur within one or two atomic layers from the surface or pores for CEC to be developed. Various cations held in a water sheath or "double layer" near such negative surfaces are exchangeable by other cations including protons ( $OH_3^+$ ) of soluble salts, acids or bases in solutions in contact with the surface.

Schollenberger and Driebelbis (89) investigated the use of a neutral 2M solution of  $NH_4$  acetate for estimation of exchangeable bases.

and supported the claim that it is the most satisfactory salt for the purpose. Jackson (45) also recommends this salt for base determination. Ammonium acetate is a neutral salt and its solution is buffered around pH 7. This makes the dissociation of both acids and bases practically equal and the ionization product is small ( $1.8 \times 10^{-5}$  at  $25^{\circ}\text{C}$ ). They recommend the leaching method as the best means of extracting cations from the soil.

Mehlich (66) proposed the use of triethanolamine acetate barium hydroxide buffer for the determination of cations exchange capacity, base and hydrogen saturation, and lime requirement of soils. A 0.2 N solution buffered at approximately pH 8.15 is advantageous for the efficient replacement of soil bases.

Mehlich's procedure (66) for the estimation of the determination of lime involves the determination of barium adsorbed by the soil (base or lime adsorption capacity at approximately pH 8.15) titratable acidity and replaceable magnesium. The barium adsorbed by the soil is determined by the difference in concentration of the test solution before and after treatment of the soil.

Truog and Bower (95) investigated the question of why clay acids, like weak acids, form salts when neutralized with weak bases of divalent cations and why; when these cations are used in the determination of base exchange, higher results are obtained. They found that base exchange capacity, when determined with polyvalent cations, was higher than when determined with monovalent cations for a Miami silt loam. Results obtained with monovalent cations were in good agreement while those obtained with divalent cations became higher with decreases in the strength of the base which their respective ions formed. They

noted that cations which form basic exchange salts are much more difficult to replace. This suggests that, Cu may be decreased in availability as a plant nutrient and may be reduced in toxicity when present in considerable amounts because of the tendency to form basic exchange salts. They believed that these results indicate a connection with the availability and toxicity of certain nutrient elements for example, copper and zinc.

#### Availability and Nutrient Requirement of Plants

Bray (21) investigated ionic competition in base exchange reactions. He considered equilibria involving small amounts of electrolyte and relatively large amounts of cation-exchange material as the most important equilibrium process in soil. He gave seven rules governing exchange competition in soils. The relative ease of release for univalent and bivalent cations is in the order  $\text{Na} > \text{K} > \text{Mg} > \text{Ca} > \text{H}$  (21).

Jarosov (48) reported where two different cations are present on a surface, the cation with the higher bonding energy occupies those positions or sites on the surface that have the greatest energy release. The one with the lower bonding energy will occupy an area with lesser energy release. This was confirmed by Jenny and Ayers (52) in 1939.

Many other soil chemists (71,92,102,103) have investigated ionic equilibria in soils and the energies of replacement of one ion by another as well as the uptake of nutrients by plants. It has been observed that (92,102) an increase in the concentration of K in a solution with a constant value of Ca, results in a rapid decrease of Ca uptake, but that the reverse is not true of potassium. Taylor (92)

found that the relationship between K and Ca ion was obeyed only in soils of low K-status.

Energy of exchange (102,103) is a measure of the intensity factor in the delivery of a balanced supply of nutrient cations from the exchange complex of the soil to the growing plants. It determines whether or not reactions will occur and also determines the nutritional balance of a suite of cations which will be exchanged from the soil. The energy of replacement of potassium (71,92,101) at which deficiency will appear in the plant has been set at 4000 calories and 35000 calories as the upper limit for the normal performance of the plants. Variations which occur in soils which have received large amounts of K-fertilizers are caused by an exchange reaction by which the amount of K in readily exchangeable form is increased as the electrolyte concentration is raised (92,102).

Mass-flow, root interception, and diffusion (71) are the three mechanisms which govern the rate of nutrient supply from the soil to plant roots. Oliver and Barber (71) found mass flow to be significant in supplying Ca and Mg but of little importance for the supply of Na and K. Increase in the mass-flow of Ca and Mg were highly correlated with increase in the uptake of Ca and Mg by the plants.

In a second experiment dealing with root interception of Ca and Mg and in which mass-flow was minimized by previous leaching of the soil, it was found that the calculated Ca uptake by root interception gave reasonably close approximation to uptake of Ca minus mass-flow Ca.

Root interception by a given plant is related to the effective soil volume per plant (102) which can be influenced by impervious soil



horizons or horizons containing toxic concentrations of elements such as aluminum and manganese. The amount of different elements removed by mass-flow is related directly to the amount of water transpired by the plant as well as other factors which also affect the amount of each ion being removed as a result of diffusion.

Baker (5) proposed that ion availability is related to ionic activities rather than ionic concentrations as described by various investigators (21,71,92,101,102,103) and the mechanism governing the supply of nutrients to plant roots as outlined by others (71,92,101,103) were in error. Baker devised a new method for testing soils which could be used for estimating the availability and requirement of nutrient elements by plants. The method is based on the amount of each element removed from the soil or the amount yielded to the soil by an extracting solution containing salts, acids, or combination of both. From the change in composition of the solution after extraction, the nutrient element requirement for plant growth can be computed. The initial experiment has as its objective the prediction of the K required to provide optimum and minimum availability of K in different soils. The study was limited to K, Mg, and Ca, with twelve different soils, and eight extracting solutions with differing chemical properties were used in this investigation.

Baker observed that all soils removed K from a solution that was conditioned to provide medium to high amounts of the element. The test was concerned with determining the low level of K availability (not deficiency) and the results indicated that only a relatively small amount of K was removed. Greenhouse studies (3 separate sets) with sufficient K for 4000 calories for the energy of exchange

on bean plants showed no response to added K.

Baker (5) believed that if the amount of K removed by these soils were applied as fertilizer an adequate level of K would be provided for field crops. He also concluded that soils which did not remove K from the extracting solutions do have sufficient K available for adequate plant growth. Another aspect of this study was the importance of the energy of exchange and the percent K in solution as a parameter for K availability. This extracting solution for this test contained  $4.8 \times 10^{-4}$  m/l KCl. It was observed that four of the soils liberated K to this solution. Two of the four soils were noted for their productivity and were also rich in the clay mineral illite.

Baker concluded that K and Mg requirements of soils can be determined directly from changes in the concentration of the respective ions in the extracting solution when soil samples are equilibrated in a soil-solution ratio of 1:10. The solution contains  $2.4 \times 10^{-4}$  m/l KCl,  $9.6 \times 10^{-4}$  m/l  $MgCl_2$ , and  $48 \times 10^{-4}$  m/l  $CaCl_2$ .

Baker (6) in a subsequent experiment modified the extracting solutions by the addition of Mn, Fe, Zn, Cu, S, and P. In order to maintain a relatively constant activity for each element in the different soil extracting solution, he incorporated the use of a preservative (0.1 gm phenylmercuric acetate in 20 ml of dioxane diluted to 100 ml.), a pH buffer DTPA, and TEA. In this test, the levels of H and Ca were held constant while these for other elements varied. Three additional soils were included in this investigation.

Baker reported excellent results and indicated that the adsorption equilibria soil test could be successfully used to test for several nutrient element requirements. He concluded that the significant soil

X solution interaction was due to the high precision for Mg and K. The rankings for the 15 soils studied were not substantially different from previous studies and Baker noted the test for two of the soils to be significantly different in K and Mg requirements regardless of the test solution used. He therefore concluded that the modification did not substantially affect the reliability of the method. The use of DTPA was found to be advantageous in testing for Mn, Zn, Fe, and Cu. The investigation showed that these extracting solutions could also be used in predicting soil requirements for lime, K, Mg, Cu, Zn, Fe, and Mn. He could not however, make conclusive predictions for phosphorus.

#### Exchange Acidity

Jackson (47) indicates that the most important chemical property of a soil as a medium for plant growth is its pH value or hydrogen ion activity. Jackson (46) and Jenny (50) have suggested that the acid principle in soils is associated with aluminum.

Jackson (46) and Jenny (50) have concluded that soil acidity is essentially due to clay saturated with complex aluminum polymers and never hydrogen ions, as such, except under laboratory conditions.

According to Jenny (50) the controversy involving aluminum and hydrogen and soil acidity came to an end in 1952 when Coleman and his coworkers compared heat of neutralization and titration curves of  $H^+$ - and Al-resins with those of H-clays and acid leached clays and Al-clays and proved that electro-dialyzed clay is aluminum clay and that aluminum saturated  $H^+$ -clays are strong acids.

Jackson (46) further elaborates on aluminum banding in soils and

points out its usefulness in understanding many properties of the soil system. He explains aluminum banding is analogous to hydrogen in aqueous systems. He discusses the solubility product of  $\text{Al}(\text{OH})_3$ ,  $K_1$  of  $\text{Al}(\text{OH}_2)^{+3}_6$ , and the Pauling  $K_1/K_2$  ratio of  $10^5$  which are applied in the calculation of concentrations of aluminohydronium monomeric cation species of valence 3, 2, and 1. These concentrations relate to the cation exchange and interlayer aluminum polymerization reactions in soils during chemical weathering. The generalized bonding equation for this and mineral colloids composition is  $\text{Al}-\text{O} \rightleftharpoons \text{Al}-\text{OH}$ . This provides an ultimate buffer function in both the lower and upper pH range of soils except in the presence of strong acid-forming compounds such as S and FeS. Jackson notes aluminum banding is central to soil acidity through not only the acidic aluminohexahydronium monomeric cations but also through the weakly acid  $\text{Al}-\text{OH}_2 \dots \text{OH}$  pair in edges of polymerized precipitated hydroxy alumina structures. Aluminium toxicity and soil acidity may involve Al-bonding and solubility product relations at the soil-root interface and in solution in the soil and in the plant sap. Retention by soil of anions such as phosphorus and sulfate is closely related to aluminum bonding of these anions (OH replacement).

Most soils in humid regions are acid (13). Many soil scientists (13,37) have shown that this acidity is brought about by excessive leaching due to heavy rainfall in these areas. Carbon dioxide from the air and soil water combined to form carbonic acid and have been postulated as the ultimate cause of acidity in soils. Plants can not grow well in extremely acid soils. As the acidity increases, past some limit depending on plant species, plant growth usually declines.

Many soil scientists (27,29,41,66,76,86,87) have developed methods to be used in estimating the amount of acids in soil and how to condition the soil for optimum plant growth. Comber (29) developed the use of potassium thiocyanate to determine lime requirement of soils. In 1933, Harper (41) studied and compared various acid-based indicators in the determination of soil reaction. He found that filtrates of indicators passing through different soils did not give the same results as did the electrometric measurements of pH values of soil-water suspensions. A study of the absorption of indicators showed that brom thymol blue and brom cresol green were absorbed to greater extent than brom cresol purple, chlor phenol red or cresol red. Brom cresol purple was found to give sharper color changes than chlor phenol red and was therefore recommended as a possible useful indicator of soil acidity.

The hydrogen ion activities and its effects on cation exchange capacity and its determination has arrested the concern of many investigators (29,41,47,76,86,87). Schofield (86) investigated the electric charges carried by clay particles and pH. He found that these charges were pH-dependent. This means as the pH of a solution surrounding a clay particle is raised, the charge on the clay is increased resulting also, in a corresponding increase in the number of exchange sites on the clay particles. For instance, he found that as the pH was increased from 5.5 to 7.4 the negative charges also increased from 24.5 to 28.2 meq/100 grams.

Coleman, Weed, and McCracken (27) investigated cation-exchange capacity and exchangeable cations and emphasized the magnitudes and sources of negative charges on the exchangeable cation populations

as related to other soil characteristics. They were concerned with the contributions of both permanent charge and pH-dependent charge. Leaching a soil sample with a neutral salt solution should remove exchangeable ions which are bonded electrostatically (27). The ions displaced by these treatments may be regarded as those neutralizing permanent charges on soil minerals. On the other hand a buffered salt solution not only displaced exchangeable ions bonded to permanent charges, but also neutralized a part of the weak acid or pH-dependent charge. These investigators prepared two different solutions (1N KCl and  $\text{BaCl}_2$  - TEA + 1N KCl) for investigating the permanent and pH dependent charge. The sum of the exchangeable Ca, Mg, and exchange acidity were regarded as reflecting permanent charges of the various soil samples. The base consumed on leaching KCl-treated soil samples with  $\text{BaCl}_2$  - TEA and pH 8.2 was taken as the pH-dependent charge measured as the base requirement on raising the soil pH from about 6 to 8.2. Ratios prepared between the results obtained from these two leachings indicated that great differences existed between the various soils tested. A soil found to have a high permanent charge at low pH but a low pH-dependent charge at high pH gave a high ratio. On the other hand, a soil found to have a low permanent charge at low pH and a low pH - dependent charge at high pH gave a low ratio. A large proportion of the CEC for soils with high ratios came from permanent charge which exists at low pH. While a large proportion of the CEC for soils with low ratios was due to pH-dependent charge which exists at high pH, they recommended a breakdown of the soil CEC into low pH and high pH components which was a more realistic appraisal of exchange characteristics. Pratt (79) confirmed the findings of

Coleman et al. He found a continuous change in the CEC of some soils as the pH was changed. Data for other soils indicated a constant value between pH 3 and pH 4.5 but increases did occur as the pH was increased from 4.5 to 8.0. He defined the pH-dependent cation-exchange capacity to be equivalent to the exchange acidity not displaced by a neutral KCl solution but displaced by a buffered  $\text{BaCl}_2$ -TEA solution.

In dealing with the problems of pH determination and lime requirements, Schofield and Taylor (87) found that a soil pH determination in a 0.01M  $\text{CaCl}_2$  could be used satisfactorily. They obtained satisfactory results especially on non-saline soils where the surface density of electrical charge on colloidal material was high and independent of the solution composition. Mehlich (66) introduced the use of  $\text{BaCl}_2$ -triethanolamine for determination of soil acidity and lime requirement. Peech et al. (76) modified Mehlich's procedure. The buffer and extracting solution used by Mehlich were replaced by a single solution which consisted of 0.5N  $\text{BaCl}_2$  and 0.05N TEA neutralized to pH 8.0 with HCl. This method gave higher results than the ammonium acetate method and the results were in better agreement with the standard residual carbonate method.

### Phosphorus

Phosphorus is classified as one of the major elements required by plants (93). It occurs in plants in quantities much smaller than either nitrogen or potassium. Plants absorb this element primarily as the orthophosphate ion  $\text{H}_2\text{PO}_4^-$  and as the secondary orthophosphate ion,  $\text{HPO}_4^{2-}$  in smaller amounts (93). Phosphorus has been recognized as a

constituent of nucleic acid, phytin, and phospholipids. Adequate supply is said to increase root growth and to hasten plant maturity.

Many soil scientists (57,74,83,100) have classified soil phosphorus into several groupings, according to its distribution in the soil and according to its solubility. Russell (83) categorized phosphorus in the soil into three main groups:

- (1) Phosphorus in the soil solution which is small as compared to other ions;
- (2) Phosphorus in the organic matter; and
- (3) Phosphorus in the inorganic form both definite phosphate compounds and surface films of phosphate held on inorganic soil particles.

The bulk of the phosphorus in the soil is in the inorganic form except for a few soils on ancient peneplains and some strongly leached tropical soils (83). In these soils, organic phosphate is the principal reserve of plant available phosphate. The importance of organic phosphate is mainly two-fold: (1) to prevent the conversion of available phosphate to the difficultly soluble form in soils low in phosphate and to speed up the build-up of a humus where grass is grown and (2) as a source of phosphate supply to plants by being converted to the inorganic and available form (83).

Kurtz (57) and Williams (100) have attempted to group phosphate compounds based on solubility. Kurtz (57) grouped phosphorus into inorganic and organic and classified the inorganic phosphorus into two groups: (1) water-soluble inorganic phosphorus which is a relatively small portion, confirming the classification of Russell, and (2) acid-soluble which is a relatively large portion. Kurtz (57) studied



acid soils and separated phosphorus into four main groups based on their solubility:

- (1) Soil phosphorus soluble in strong concentrated acid;
- (2) Soil phosphorus soluble in dilute acid dissolves in 0.2N nitric: hydrochloride;
- (3) Adsorbed phosphorus and phosphorus soluble in alkaline solution which dissolve in NaOH such as the apatite type;
- (4) Residual phosphorus or phosphate which is inert to extracting reagents.

Williams' (100) solubility classification was based on phosphorus behavior in sodium hydroxide. He grouped phosphorus compounds into three main areas more or less similar to that of Kurtz:

- (1) Soluble-phosphorus in combination with sesquioxides, organic phosphorus, exchangeable phosphorus of the clay complex, phosphorus of calcium compounds such as  $\text{CaHPO}_4$ , and phosphorus of water-soluble compounds;
- (2) Insoluble-phosphorus in compounds of the apatite class;
- (3) Doubtful-phosphorus in the interior of the clay structure and phosphorus of titanium compounds.

It has been observed that calcium phosphate is the predominate phosphate compound in alkaline and calcareous soils while iron and aluminum phosphates are of equal or greater significance in acid soils (57).

Olson (74) found that phosphate in alkaline and calcareous soils occurs in the form of hydroxyapatite, fluorapatite, chloroapatite, wagnerite and wavellite, and in organic forms. He found that alkaline and calcareous soils were dominated by calcium phosphate while iron and

aluminum phosphate were dominant in acid soils. Chai and Caldwell (26) studied the forms of phosphorus fixation, and availability and characterized the organic and inorganic phosphates. They divided inorganic phosphate into aluminum, iron and calcium compounds. Their fractions were in agreement with Olsen in that iron and aluminum compounds of phosphorus are characteristics of acid soils while calcium compounds were characteristic of alkaline soils. They found that soils with pH near 7 all three inorganic phosphate compounds were evenly distributed. Phosphate-fixing capacity was found to increase with departure from a pH near neutrality. Organic phosphate was found to be positively related to the content of soil organic matter. The amount of soluble phosphorus as determined by methods employing strong acids were found to be higher than those using weak acids.

The tendency of phosphorus to be present in the soil in nearly insoluble compounds is largely responsible for phosphorus deficiency soils and decreased plant growth on many soils. Many scientists (28,34,39,59,68) have investigated soil phosphorus and come to the conclusion that fixation of phosphate is mostly due to the clay minerals, especially Kaolinite clay, in the soil.

Murphy (68) in defining fixation of phosphate said, "when a soluble phosphate is brought into contact with the soil, reactions take place which remove a great deal, if not all of the phosphate from the solution. This phenomenon has been called fixation of phosphate by soils". He found that soils with a kaolinite type of clay have a high capacity to fix soluble phosphate. This clay when in a colloidal form has a high fixing capacity. The fixation is greatest at acid reactions which indicates that the  $\text{H}_2\text{PO}_4^-$  ion is the most favored phosphate ion for the

reaction. An increase in base-exchange capacity accompanies the increase in phosphate fixed. He showed that the availability of the phosphate in "kaolinite phosphate" is directly proportional to the degree of phosphate saturation. This means that a light phosphate fertilizer application might be ineffective on soils having a kaolinitic kind of clay.

Law and Black (59) were concerned with the fixation of phosphate by kaolinite and the effect of phosphate on kaolinite clay. The study was based on the hypothesis that kaolinite dissociates into aluminum and silica ions and that phosphate precipitates the aluminum ion thereby disturbing the equilibrium and causing the clay to dissolve in accordance with solubility product principles. As evidence of this hypothesis, they found that the addition of both phosphate and 8-hydroxyquinoline to kaolinite produced a considerable increase in the concentration of silica in the solution, whereas, ammonium chloride caused only small increases in dissolved silica. Moreover, extraction of the phosphate kaolinite with ammonium oxalate caused the liberation of aluminum and phosphorus in a constant ratio despite variations in time of extraction and quantity of fixed phosphorus in the clay. From these results they concluded that phosphate in the phosphated kaolinite was present as an "aluminum phosphate" and not as a "kaolinite phosphate".

Hemwall (42) investigated the role of clay minerals in phosphate fixation. He discovered that phosphorus is fixed by clay minerals by reacting with insoluble aluminum which originates from the exchange sites or from lattice dissociation of the clay minerals to form insoluble aluminum phosphate compounds. His experiments showed that

the insoluble aluminum-phosphate was variscite ( $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ ). The rate of fixation is dependent upon the rate at which the clay replenishes the solution with soluble aluminum. Reaction was slow with lattice-associated aluminum but rapid with exchangeable aluminum.

Fixation of phosphate has been noted to be greater in acid soils than in calcareous soils. Ghani and Islam (39) investigated phosphorus fixation on acid soils. Based on incubation with optimum moisture content and fractionation of samples at periodic intervals, they reported: (1) as the amount of phosphate added increased the available phosphate also increased but not in the same proportion; (2) as the time of contact between the P compound and the soil increased, the available P tended to increase for two weeks then remain constant, (3) as the amount of P added increased, the amount of P fixed also increased. However, about 70-95% of the phosphates were fixed by the 6th week of incubation. The percentage of phosphate fixed at any time was lower at a higher rate of application. The amount of P fixed in the different treatments was highly correlated with the phosphate recovered as iron and aluminum phosphate. More than 90 percent of the P recovered was as iron or aluminum phosphate; and no phosphate reverted to apatite form.

Perkins (77) reported that regardless of pH, increase in cation-phosphate ratio increased the percentage of phosphate precipitation. However, one-third calcium plus one-third iron with two-thirds and three-thirds of these mixed cations do not precipitate the phosphate. He also observed that calcium shows a general increase in phosphate fixation from pH 2.5 through pH 9.5 except when in minimum amount equivalent to one-third of the phosphate. With magnesium, fixation

increased from pH 2.5 to 4.5 and from pH 4.5 to pH 9.5 phosphate fixation gradually decreased.

Coleman (28) reported that the phosphate held by the coarse clay and most of the phosphate held by the fine clay was fixed by the free iron and aluminum oxides. He used hydrogen- and aluminum-saturated clays at different reactions both before and after the free iron and aluminum oxides were removed. Kaolinite and montmorillonite in the fine clay fixed appreciable amounts of phosphate but the kaolinite, montmorillonite, quartz, and mica in the coarse clay minerals were unable to fix phosphate. Phosphate fixation by both fine and coarse clays is influenced by reactions and exchangeable cations only as long as the free iron and aluminum oxides are present. The activity of these free oxides determines the amount of  $PO_4$  fixed by the clay. The amount of  $PO_4$  fixed by clays is influenced not by the type of clay minerals, but by the amount and activity of the free oxides of the Fe and Al.

Recovery, transformation and availability of phosphate to plants has been an area of great interest. Dickman and Bray (34) reported that adsorbed added phosphate could be recovered by shaking 1 gram of kaolinite with 50 ml. of 0.1 N neutral  $NH_4F$  for one minute. They observed that continued phosphate-kaolinite contact, drying, and calcium saturation tended to decrease recovery of added phosphate by this method.

Dalton et al. (30) worked on the effect of organic matter phosphate availability to plants under acid conditions and reported that organic matter added to soil as an amendment is effective in increasing the availability of soil phosphate to plants. Easily decomposable organic

matter was more effective than that which decomposed slowly. They attributed the ability of organic matter in making  $PO_4$  available to the ability of certain metabolic products of microbiological decomposition to form stable complex molecules with Fe and Al that are responsible for  $PO_4$  fixation in acid soils.

Basak and Bhattacharya (9) studied phosphate transformation in rice soil (paddy). Their investigation showed that waterlogged soils tend to possess a unique capacity of regenerating an increasing quantity of available phosphorus during the growing period of the rice plant. They believed that the source of the phosphorus supply and the causes of its regeneration was probably due to the release of phosphorus by mineralization of organic phosphorus and reductive transformation of iron and aluminum phosphate under anaerobiosis due to waterlogged.

Al-Abbas and Baber (1) used phosphorus uptake by millet as an indication of phosphorus response, and correlated these data with a  $NaOH-Na_2C_2O_4$  extractions procedure to determine extractable  $PO_4$ . They reported  $Na_2C_2O_4$  to be superior to five different extractants by comparison and it was more effective at pH values above 7. In a second test (2) involving multiple regression analysis, they correlated the soil phosphorus fractions with plant-available phosphorus. It was observed that iron phosphate was significantly correlated with available phosphate.

Nye and Bertheux (68) investigated the phosphorus status of forest and savannah soils in the Gold Coast (Ghana). They reported that forest soils have more total phosphorus and more organic and inorganic phosphorus than savannah soils. The carbon-phosphorus ratio was found

to average 233 in forested soils and 247 in savannah soils. The higher content of P in forest soils was probably due to high organic matter resulting from forest litter. Total phosphorus was found to be greatest at the surface of forest soils and no consistent change was observed in savannah soils.

Bates and Baker (11) reported the accumulation of soil phosphorus in the subsurface of some Nigerian soils. Below 2 inches, the profile exhibited a marked decrease in total phosphorus content, indicating a large decrease in organic phosphorus. Thereafter, total P was observed to be fairly constant down the profile. About 80 percent of the total P in the gray horizon (12-30 in.) was immobilized in iron concretions. There was little Ca-bound phosphate below two inches.

Hesse (44) examined some muds from mangrove swamps in Sierra Leone and found no aluminum-bound phosphate despite a high (5 percent) dilute acid extractable aluminum content. This was true even where added calcium phosphate had been immobilized in the mud. The distribution of total P in this mud was 87 percent in organic form and the remainder in association with iron and calcium. Hesse holds that the absence of aluminum bound phosphate in the mud appears to be due to a transfer to iron of any phosphate which may have been acquired by aluminum.

Many soil scientists (22,35,67,84,94,100) have developed methods dealing with the determination and extraction of the various forms of phosphorus. Truog and Meyer (96) developed a modification of the Deniges method of developing blue color when stannous chloride is added to a molybdate of phosphorus or arsenic. They found that ferric iron when present in concentrations greater than 6 ppm markedly

depresses the formation of the blue color and also gives rise to greenish tints. Reduction to the ferrous condition is said to eliminate this hazard. Titanium may be present up to 20 ppm without interfering with the color. Salts of Al, Mn, Ca, and Mg may be present in large amounts without causing undue interference. Nitrates may be present in large amounts without interfering. They recommended:

- (1) Preparation of a stock solution of stannous chloride by dissolving the pure salt in acidified water and preserving it by covering with a layer of white mineral oil and
- (2) doubling the amount of ammonium molybdate and increase the acidity.

This makes the method more sensitive and the full effect of all the phosphorus is brought into play.

Dickman and Bray (34) described a colorimetric method for phosphate determination. The methods employ a molybdate-hydrochloric acid solution instead of a molybdate-sulfuric acid solution. The method is not affected by chlorides or by ferric ion up to 15 ppm. Color fading is less rapid than with most methods. It is applicable for phosphate determinations in soils, water analysis, oceanographic analysis, plant analysis in which the sample is taken up in HCl and for biological tissue determinations.

Watanabe and Olsen (75) recommend the use of the isobutyl alcohol method for colorimetric determination of phosphorus. They claimed that this will prevent the interference from dissolved organic matter or some materials adsorbed by carbon black.

Truog (94) recommended the Deniges colorimetric procedure to facilitate the rapid and accurate determination of readily available



soil phosphorus. His extracting solution was 0.002 N  $\text{H}_2\text{SO}_4$  buffered with ammonium sulfate to a pH of 3. He used a soil solution ratio of 1:200 which should minimize refixation of dissolved phosphate due to the low concentration. He recommended that this concentration makes it possible to maintain a more constant strength of the solvent and to imitate plant feeding during the extraction process. He found that extraction with 0.002 N  $\text{H}_2\text{SO}_4$  buffered to a pH of 3 completely dissolved finely ground rock phosphate in one hour and powdered apatite in several hours. He also found that powdered sulfrenite gives up a trace of phosphorus to this solvent.

Bray and Kurtz (22) worked on the extraction of the various forms of phosphorus and adopted the use of perchloric acid digestion for total phosphorus as suggested by previous workers. They claimed that this method can be applied in a semimicro way if desired, that the phosphate is determined directly in an aliquot from the original digestion and that arsenic and iron do not interfere when present in appreciable but not excessive amounts. They also developed a method for a rapid determination of soil phosphorus depending on its solubility. They proposed the use of 0.03 N ammonium fluoride and 0.025 N hydrochloric acid solution for extraction and concentrated molybdate reagent and a tin rod as a reducing agent. For the determination of acid soluble and adsorbed phosphorus, the above reagents except HCl were recommended.

Mehta et al. (67) developed a procedure for determining organic phosphorus. This procedure consists of successive extractions with concentrated HCl and 0.5 N NaOH at room temperature and 0.5 N NaOH at 90°C. The difference in content of inorganic and total phosphorus in

the combined extracts was taken as total organic phosphorus in the soil. Saunder (84) also proposed the use of hot 0.1 N NaOH as a reagent for extraction of available phosphorus from tropical soils, particularly red earths, where P is retained in the soil in very insoluble forms. Only the inorganic fractions is determined and the organic fraction is separated by acidification.

#### Organic Matter and Nitrogen

The organic matter in the soil is initially derived from the green plants living in it (13). These plants and their residues are decomposed to CO<sub>2</sub> and water. The residue of this composition gives the soil a dark color and the dark material is called "humus" (13). Bear (13) defined organic matter as that which "consists of plant residues at various stages of decomposition along with its corresponding products at decomposition and excretion of all the micro-organisms living in and on the soil".

According to Russell (83) both Achard and Vaquelin in 1786 attempted to extract the soil humus. Sprangel as reported by Russell (83) distinguished the acid humus of peat formed where bases are lacking from the less acid "mild humus" formed in soils in the presence of basic materials in 1826.

Bremner and Lee (24) showed that neutral sodium pyrophosphate is effective in dispersing significant amounts of humus up to 20-30 percent of the organic carbon in the soil. Its advantage lies in the fact that it produces no organic anion.

The elements carbon, hydrogen, oxygen, nitrogen, phosphorus, and sulfur are major constituents of humus (37,47,83). Russell (83)

reported that about 58-60 percent of the soil humus is carbon. He gave the carbon, oxygen, and hydrogen ratio of humus as 100:55:7. The carbon:nitrogen ratio of the organic matter is determined for the purpose of assessing the influence of organic matter on plant growth.

The C/N ratio in soils is higher for soil organic matter produced under acid than under neutral conditions (87). In a soil profile the C/N ratio decreases with depth (83). The organic matter content of a soil increases at the rate at which plant remains are added (83). Forest soils have the bulk of their organic matter close to the soil surface while prairie soils by contrast, have a greater proportion of their organic matter in the deeper horizons.

The rate of decomposition of the organic matter depends on soil aeration, calcium supply, and temperature. Well aerated soils with an adequate calcium supply favors a rapid rate of decomposition of organic material (83). It has been reported that acid soils with small animal populations usually have higher organic matter in their surface layers than in surface layers of well drained neutral soils (83). Higher temperatures favor a rapid rate of decomposition due to the vigorous activities of soil microorganisms.

In the United States organic matter content of the temperate zone soils increases with increasing rainfall and decreasing temperature (38). The former favors plant growth and the latter retards the rate of decomposition.

Fowler and Wheeting (38) studied forest soils in Washington with an ambient environment of uniform temperature and humidity but different in rainfall. They reported that organic matter varies in different soils. The C:N ratio is wide under high rainfall and narrow under low

rainfall.

Jenny (51) investigated the organic matter and nitrogen content of two tropical soils of Columbia and Costa Rica and compared them with those of California, a subtropical-humid region. He found that organic matter and nitrogen content of these soils were higher than those of California. This is contrary to the existing belief that tropical soils are low in organic matter and nitrogen. He also reported that the proportion of carbon to organic matter in the tropical forest floor with a high litter fall to about 0.6 percent for the oak forest and 1.8 percent for the pine forest. This value was higher for the California profile with 11.0 percent for oak forest and 37 percent for the pine forest.

Norman (69) reports that in the low, hilly lands of the tropics conditions are optimum for mineralization of plant residues. This results in little organic matter accumulation either in the original or transformed state. At elevations above 1,000 meters with good moisture and aeration the humus content increases.

Benavides (14) fractionated some tropical soils of Columbia and found organic matter content to be 4.59 percent in the first 4 centimeters of depth decreasing with depth to 0.04% for the 150 cm layer. Nitrogen content corresponding to these depths was 0.28% and 0.01%: C/N ratio being 9.5:1 and 4:1.

Many attempts (24,58,88,98) have been made to develop methods by which percent organic matter in the soil can be determined. Walkley and Black (98) introduced the use of potassium dichromate and concentrated sulfuric acid for the digestion and determination of organic matter.

Schollenberger (88) developed a method involving potassium dichromate, concentrated sulfuric acid, heating to  $175^{\circ}\text{C}$ , titration with 0.2 N ferrous ammonium sulfate, and with an indicator compound, sodium fluoride powder and diphenylamine in concentrated  $\text{H}_2\text{SO}_4$ . Lee (58) also described a method for organic matter determination for paddy soils.

Jackson (47) classified soil organic matter extraction into two types:

- (1) treatment in dilute alkali, alcohol metaphosphate, or HG and
- (2) treatment with strong NaOH.

Schnitzer and Levesque (85) found 0.4 to 0.5 N NaOH as a suitable extractant for obtaining the soil organic matter content. They found the extract to be low in ash content.

The uptake of nitrogen by plant roots surpasses that of all other elements required by plants. It is usually absorbed in the nitrate form. The quantity of nitrogen in the soil is closely related to the amount (12,13,83) of soil organic matter. Mineralization of soil nitrogen is the process by which nitrogen in the organic form is converted into the inorganic ammonium and then by nitrification, to nitrate ions for plant use. The stages in this mineralization is probably organic N  $\longrightarrow$  ammonium  $\longrightarrow$  nitrite  $\longrightarrow$  nitrate. Nitrogen compounds in the soil are derived from protein synthesized by the soil organisms living in the soil or the plants living on the soil. Nitrates, nitrites, and ammonia usually make up less than one percent of the nitrogen in mineral soils (13). Bear (13) reports the C/N ratio of well decomposed organic matter to range from 10:1 to 12:1.

Carbon content of this organic matter is about 50 percent by weight. Most mineral soils contain between 1-5 percent organic matter and the nitrogen content on an air-dry basis is between 0.05 and 0.25 percent.

Russell (83) has divided the nitrogen compounds in the soil into three main categories:

- (1) nitrogen present as nitrate or ammonium ion which accounts for more than 1 to 2 percent of the total nitrogen and which forms a primary source of nitrogen for plant;
- (2) nitrogen in compounds that decompose readily to give ammonium or nitrate ions known as nitrifiable nitrogen compounds; and
- (3) nitrogen present in compounds that are slowly decomposed by the soil microbial population.

The amount of nitrogen in the soil available to the plant during the growing season depends on the rate of nitrate production in the surface soil during the season and also on the amount of nitrate produced in the previous season and stored in the subsoil within the range of the plant roots. The rate of nitrate production in the surface soil depends both on the amount and nitrogen present in the readily oxidizable organic matter present and the rate of oxidation. The rate of oxidation is rapid in most well aerated soils.

Climate (83) is a factor related to the amount of nitrate stored in the subsoil and the depth from which plant roots can extract it.

Jenny et al. (52) examined soil samples from an equatorial region of Columbia, and the Great Plains of the United States both of which have the same temperature and rainfall. They found that at high temperatures and low latitudes, soil nitrogen and organic matter increase as

precipitation became higher. From sea level to higher altitudes nitrogen and organic matter increase. For belts of constant rainfall the nitrogen content increases exponentially as temperature decreases. In a comparison, the Columbian soils were found to have much more nitrogen and organic matter in the surface soils than the North American soils.

Dean (33) found the subtropical soils of Hawaii to be rich in nitrogen as compared to temperature zone soils. The mean nitrogen content averages about  $0.31 \pm 0.004\%$  and the mean organic matter content was  $3.75 \pm 0.03\%$ . The correlation coefficient between nitrogen and organic matter was 0.74. Assuming a factor of 1.72 for carbon to organic matter, the average carbon percentage was 2.18 and the C/N ratio 7 to 1.

Dean (32) reported the following results on nitrogen and carbon contents of Hawaiian soils: (1) Carbon content increases with increasing nitrogen, rainfall, and elevation. (2) The nitrogen content increases with increasing carbon, rainfall and elevation but with constant carbon content, nitrogen decreases with increasing rainfall and is not significantly related to elevation. The carbon-nitrogen ratio of soils increases with increasing rainfall but is not significantly related to elevation.

The source of nitrate in tropical rain water has been traced to fine dust particles and photochemical reactions occurring in the atmosphere by Visser (97) who worked in Uganda.

Many methods (23,63,80,99) have been developed for the determination of total nitrogen compounds in the soil. Prince (80) presented methods for the determination of total nitrogen, ammonia, nitrites, and

nitrate in the soil. Total nitrogen determination was based on the Kjeldahl method. Ammonia was determined at ordinary temperatures by aerating a suspension of the soil with a 4 percent solution of  $K_2CO_3$  and a 20 percent solution of KCl. Ammonium hydroxide is added in the case for nitrate extraction.

McLean (63) attempted to measure the nitrogen supplying power of soils by extraction with sodium bicarbonate. He presented four methods for accomplishing this:

- (1) microbiological methods in which N mineralized during a certain period (1-2 weeks) of incubation is measured;
- (2) total nitrogen;
- (3) mineral nitrogen content of fresh samples;
- (4) nitrogen mineralized as a result of chemical treatment involving acid or alkaline hydrolysis.

He used total nitrogen supplying power and also those of chemical treatment. In a greenhouse experiment, through direct nesslerization he used sodium bicarbonate to measure the nitrogen supplying power of soil. He found the relationship between soil nitrogen values by this method and nitrogen uptake by ryegrass to be superior ( $r = 0.76$ ) to all other previous methods studied.

Waring (99) developed a rapid method for determining mineralizable nitrogen in soils. This method was based on the production of ammonium ion during incubation under waterlogged conditions. The value of the procedure is taken as an index of the nitrogen availability for plants. It has advantages over aerobic mineralization. It is simple, rapid, and reproducible. However, according to Bremner (23) only two methods have gained general acceptance for determinations of total



nitrogen: (1) the Kjeldahl method which is essentially a wet-oxidation procedure, and (2) the Dumas method which is a dry-oxidation (i.e. combustion) technique.

### Clay Minerals

Clay minerals (13,16,25,47,61) have been found to have a profound influence on the physical and chemical properties of soils. Identification characterization and understanding of these minerals and their properties is an indispensable aid in the evaluation of soils with regards to their classification, agronomic potential and engineering properties. Stelly (91) outlined ten contributions of mineralogy to soil chemistry and fertility.

According to Bear (13) and other investigators (37,54,55,56,73) the clay minerals found in soils includes kaolinite, montmorillonite, halloysite, illite, chlorite, vermiculite and mixed layer minerals. Minerals of the kaolinite, montmorillonitic, and illitic groups are most common in soils. All of these minerals according to Mason (61) are hydrous-aluminosilicates of sedimentary origin.

Kaolinite  $(OH)_8Al_4Si_4O_{10}$  is said to have an electroneutral structure (13,25,61,73). Replacement of Si and Al by other elements is not possible because atomic charges in the structural unit are balanced. Kaolinite is referred to as a 1:1 layer clay (13,25). According to van Olphen (73) the CEC of this mineral falls in the range 2-10 meq/100 grams of soil. Kaolinite is said to have the narrowest Al:Si ratio of all clays (13,73) and its formation is favored by an acid environment and is protonated if weathering tends to remove Si in solution, thereby enriching the aluminum fraction

(13,61).

Montmorillonite is referred to as a 2:1 lattice mineral. The units are stacked one above another in the direction of the c-axis and are loosely held together with water molecules present between them (13,61,73). The unit cell (13,25,73) varies depending upon the water content. Characteristics of the mineral is its interlayer swelling capacity which allows water to move between the layers and also permits ionic substitutions. Substitution of ions in the structure at the time of synthesis include Al and P for Si and Mg, Fe, Ni, and Li for Al (13). According to van Olphen the CEC of montmorillonite lies between 80-100 meq/100 grams of clay. Bear (13) reports that the CEC lies between 80-150 meq/100 grams of clay (13,73).

The structure of illite is similar to that of montmorillonite except that in the illite more of the silicons are always replaced by Al. The excess charges resulting from this substitution are compensated for by K ions that exists between the silica sheets of successive units (13). K ions act as a binding unit to prevent expansion in the presence of water. Van Olphen (73) reported the CEC of illite as 20-40 meq/100 grams.

Kelley (54) has listed several methods by which clay minerals can be identified. These methods include:

- (1) x-ray analysis
- (2) dehydration or heating
- (3) differential thermal analysis
- (4) optical
- (5) electron microscope, and
- (6) Chemical analysis and cation exchange

determination.

Black (16) has pointed out that x-ray diffraction is one of the most useful of these methods.

According to Jackson (47) diffraction analysis reveals the arrangements of the atoms, ions, and molecules within a crystal known as "crystal structure". The concept of isomorphism in atomic stacking modified the law of definite elemental proportion of solid chemical substances. Jackson (47) explains that the x-ray spectrum extends from 0.5 to 100A, but the wave length of most interest in clay mineral diffraction analysis extends from about 0.4 to 2 or 3A. The basic phenomenon of x-ray diffraction analysis is the diffraction by atomic planes in a crystal through an angle which is quantitatively related to the distance (d) of separation of the atomic planes. Diffraction can occur only when the Bragg Law  $n\lambda = 2d \sin \theta$  is satisfied (16,47).

n = order of reflection and only has integral values

$\lambda$  = wavelength of the x-ray in Angstroms

d = distance in Angstroms between atomic planes  
in the crystal

$\theta$  - angle of diffraction

Black et al. (16) have indicated that soils always contain a number of mineral species and that many of these species can easily be identified by their distinctive diffraction maxima from a single x-ray pattern. Layer-silicate species, however have many similar structural features which make their differentiation and identification more difficult.

A diffraction spacing (001) of approximately 14A obtained from

a Mg-saturated, air-dried sample may be due to montmorillonite, vermiculite, or chlorite, or by a mixture of species (16). Glycerol solvation allows separation and identification of montmorillonite while K-saturation facilitates separation of vermiculite from chlorite which does not collapse on heating.

Heating has been recommended as another means of differentiation and identification of these layer-silicates. Heating a sample to 500°C is said to serve two main functions. It effects the collapse of vermiculite which contains nonexchangeable interlayer aluminum hydroxy complexes, and secondly it destroys the kaolin minerals. Chlorite if present in a sample yields a second-order maximum of kaolinite (7.15A). If a 7.15A spacing, obtained from an unheated sample disappears or decreases in intensity after heating at 500°C, the presence of kaolinite is confirmed (16).

Kaolinite can be expanded to 14A with intersaturation with potassium acetate (16). When the potassium acetate is replaced with  $\text{NH}_4\text{NO}_3$ , a spacing of 11.6A results with kaolinite (16).

Black et al. (16) have discussed the diffraction effect on interstratified mixtures of layer-silicate species. Regular alternation of two species within a crystal produces repeating diffraction planes at distances equal to the sum of the (001) distances of the two species. Therefore a regular alternation of Mg-saturated montmorillonite and mica, chlorite and mica, or vermiculite and mica yields a diffraction spacing of 24A. (14A + 10A in each case). Regular alternation of montmorillonite with either chlorite or vermiculite, or of chlorite with vermiculite gives a spacing of approximately 28A (14A + 14A in each case).

Kunze and Jeffries (56) by saturating 15 samples of Gray-Brown podzolic surface soil clays (0-6) with potassium and then divalent cations were able to separate the potassium fixing soil-clays from the non-potassium fixing soil-clays. They reported that the potassium fixed clays showed strong 10.0A lines when saturated with potassium as contrasted with a strong 14A line when saturated with a divalent cation. They also observed that the poor potassium fixers did not change their basal spacing towards a 10A line when saturated with potassium.

## CHAPTER III

### MATERIALS AND METHODS

A. Soils: The soils for this study were collected from the northwestern sector of Liberia. They were obtained from areas which have been farmed and perhaps have received some chemicals in the form of fertilizers. However, there was very little previous information available on these samples. It should be noted that no care with regards to horizon identification was observed in collecting these samples. Each sample is therefore identified by the depth of the soil profile from which the sample was taken.

Annual rainfall for Liberia varies between 60-80 inches per year with a warm tropical climate. Savannah type vegetation intermingled with bush is the characteristic of the vegetation. The landform is flat to plateau-like. The samples represent upland soils. A complete description for these soils follows in the appendix.

#### B. Laboratory Procedure:

##### a. Physical Properties:

(1) Mechanical analyses: particle size distribution was determined by use of the Bouyoucous (20) hydrometer and it was performed on samples grouped for mineral analyses.

(2) Color: Color was determined by use of the Munsell color chart.

(3) Texture and Consistence: These were determined by

feel between the thumb and forefinger both dry and moist and by the hydrometer. The results are given in the appendix.

b. Chemical Properties:

(1) Soil Reaction: pH was determined with the corning pH Meter Model 7, using 1:1 water soil mixture and 1:1 1NKCl mixture.

(2) Cation Exchange Capacity: This was determined as described by Jackson (45). Five grams of soil were saturated with 100 ml 1N  $\text{CaCl}_2$  in four washings. The excess chloride was removed by washing with water and then 95% ethanol. The exchange calcium ( $\text{Ca}^{++}$ ) was displaced by  $\text{Na}^+$  in four washings with 25 ml of 1 N NaCl. The centrifugate was buffered with 10 ml of  $\text{NH}_4\text{Cl-NH}_4\text{OH}$  buffer. The heavy metals were complexed by use of 1 ml of a 2% solution sodium cyanide (NaCN) and 10 drops of Eriochrome Black T indicator was used. The solution was titrated with a 0.0066 N standardized EDTA solution to a bright blue color. Total calcium was assumed to represent total CEC and was calculated as:

$$\frac{\text{ml EDTA} \times \text{N EDTA} \times 100}{\text{wt. of soil (5 gm)} \times 1} \left( \text{or any fraction of } \frac{100 \text{ used in titration}}{100} \right) = \text{Meq/100 gm.}$$

(3) Exchange Cations: The exchangeable cations were determined by extraction with 1N  $\text{NH}_4$  acetate as described by Priyanishnikov, Schollenberger and Simon, and Baurer et al. as described by Jackson (45). This solution is said to be effective in wetting the soil and replacing the exchangeable cations, and is also suitable for use with flame emission and atomic absorption determination. Five grams of soil were slowly leached with 200 ml of ammonium acetate and the respective cations were determined on the Perkin-Elmer #303

atomic-absorption spectrophotometer. Each ion was calculated from the value obtained from a prepared standard curve of the element in ppm. and this was converted to milliequivalent per 100 grams of soil.

The formula used for this was  $\text{Meq}/100 \text{ grams} = \frac{\text{Grams} \times 200 \times 100}{\text{Wt. of Sample} \times \text{Meq. Wt.}}$

Note:  $\text{PPM} \div 1,000,000 = \text{grams}$ .

(4) Soil nutrient availability and nutrient requirement of soil for optimum plant growth. This aspect of the study deals with the native fertility of a soil and the amount of added nutrients that would be required for optimum plant growth. It was based essentially on the method developed by Baker (5,6). The extracting solution used in this study was patterned after that of Baker's solution No. 6 (6). As mentioned earlier, the extracting solution was conditioned by supplying it with a given quantity of each element to be tested for. The elements considered in this study were K, Mg, Ca, Mn, Fe, Cu, P, and Zn. The amount of each element in the test solution is listed in Table I.

Standard solutions for each element considered in this investigation were prepared and included even amounts of the elements included in the extracting solution. The metallic cations were determined by use of the atomic absorption spectrophotometer and phosphorus by the Bray procedure with color development according to the Murphy (68) procedure.

(5) Exchangeable acidity: Exchangeable acidity was determined by the method developed by Mehlich (66) as described and modified by Peech, Cowan, and Baker (76).

(6) Organic Matter: The percent organic matter was determined by the methods developed by Walkley (98) as presented by



TABLE I  
BAKER'S SOLUTION NO.  $6 \text{ M} \times 10^4$

Composition		Amount in grams/7 liter
KCl		.02611
$\text{K}_2\text{HPO}_4$		.1226
$\text{CaCl}_2$		2.6438
$\text{Mg Cl}_2$		.4184
Triethanalamine (TEA)		1.483 (0.32 ml.)
DTPA Diethylenetriaminepenta acetic acid)		0.557
	PPM	
Fe as in $\text{FeCl}_3$	3.0	.021
Mn as in $\text{MnCl}_2$	3.0	.021
Cu as in $\text{CuSO}_4$	0.25	.00175
Preservative (Phenylmercuric acetate)	1.0	3 drops

Jackson (45), Richards (82) and Schollenberger (88). The soil organic matter was digested with potassium dichromate and concentrated  $\text{H}_2\text{SO}_4$ . The digested sample was diluted with distilled water and excess dichromate was titrated with a 0.1257 N ferrous Ammonium sulfate. The percent organic matter was calculated by the formula: (Blank titration-sample titration) X (N of FAS) X 1.25. Percent organic carbon was derived as follows: % Organic matter  $\div$  1.72.

(7) Percent total nitrogen. The percent of total nitrogen in these soils was determined by the macro-Kjeldahl method

as described by Bremner (23) and Jackson (45).

(8) Phosphorus determinations: (a) Total phosphorus was determined by the method described by Olsen and Watanabe (75).

(b) Available phosphorus was determined by the Bray and Kurtz's (23) method. Ascorbic acid was used for color development, Murphy (68).

(c) Organic phosphorus was determined by the method of Mehta et al.

(67). One gram of soil was extracted with 10 ml of concentrated HCl and heated for ten minutes. Additional 10 ml of the acid was added and the samples were allowed to remain at room temperature for 1 hour. The sample was then diluted by addition of 50 ml water and centrifuged. Each sample was afterward extracted successively with 30 ml of 0.5 N NaOH at room temperature and 60 ml of 0.5 N NaOH after heating at 90° for 8 hours. Total and inorganic phosphorus were determined separately and the difference of the two was taken as total organic phosphorus.

(9) Mineral Analysis: The analysis of these soils for the common clay minerals was by x-ray diffraction. Each soil sample was soaked with a 2%  $\text{NaCO}_3:\text{NaHCO}_3$  solution at pH 9.0. The soil- $\text{NaCO}_3:\text{NaHCO}_3$  suspension was allowed to set for 24 hours. These suspended samples were dispersed by use of ultra-sonic generator. The samples were then poured into a soil (1000 ml) cylinder and the sand, silt, and clay fractions were determined by Bouyoucos hydrometer procedure. Excess organic matter was removed by the addition of sodium hydrochlorite (ordinary chlorox) and heating for several hours. The clay fraction was separated from the sand and silt portion by beaker sedimentation as outlined by Jackson (47). The fine clay (0.2 $\mu$ ) was separated from the coarse portion (2-3 $\mu$ ) by highspeed centrifugation in a supercentrifuge. Both of these fractions were

saturated with  $\text{CaCl}_2$  and the excess chloride removed by several washings with distilled water and then with 95% ethanol. K-saturation was also performed in a similar manner using 1N  $\text{KCl}$ . X-ray slides were then mounted for clay mineral identification by x-ray diffraction. K-saturated samples were heated to  $500^\circ\text{C}$  for confirmation of Kaolinite clays.

## CHAPTER IV

### RESULTS AND DISCUSSION

#### Particle Size Distribution

The particle size distribution analysis by the hydrometer did not involve every sample included in this study. Two or three samples of the surface soil and subsurface layers of a soil profile were combined for this purpose. These samples were later used for clay mineral analyses. In grouping these samples, emphasis was placed on combining the parts of the soil profile that were considered to be of agricultural importance and the subsurface samples were considered to be of importance for a study of the mineral characteristics of the parent material. The results of the analyses are reported in Tables II - X. The sand and clay fractions dominate these soils in all profiles. The large content of sand in these soils is probably due to cementing together of the fine silt and clay fractions by iron oxide and hydrated aluminum oxides and colloidal silica as reported by Russell (83). These large particles, called pseudo-sand grains, behave like sand. Another reason for the high content of sand could be attributed to the extreme resistance of the quartz like sand to chemical weathering. Both Mason (61) and Foster (36) have reported on Bowen's Reaction Series which shows that sand as quartz forms at the lowest temperature in a basaltic magma. It is the last mineral to be crystalized and also the last to breakdown under chemical weathering. The high clay content of

TABLE II

PARTICLE SIZE DISTRIBUTION: COMASADU I AND DALIN II  
 SAMPLES USED IN MINERAL ANALYSIS

Sample No. Depth Cm.	1 + 2 0 - 20	3 + 5 50 - 90	6 (Dalín) 0 - 26
% Sand	48	44	56
% Silt	18	12	24
% Clay	34	44	20
Textural class	Sandy clay loam	Loam	Sandy clay loam

TABLE III

PARTICLE SIZE DISTRIBUTION: FOYA MODEL III SOIL  
 SAMPLES USED IN MINERAL ANALYSIS

Sample No. Depth Cm.	33 - 60	60 - 120
% Sand	42	38
% Silt	8	6
% Clay	50	56
Textural class	Clay	Clay

TABLE IV  
 PARTICLE SIZE DISTRIBUTION: FOYA DEEP IV SOIL  
 SAMPLES USED IN MINERAL ANALYSIS

Sample No.	10	11	12 + 13	14
Depth Cm.	0 - 8	18 - 38	38 - 105	105 - 140
% Sand	54	52	46	48
% Silt	6	8	6	6
% Clay	40	40	48	46
Textural class	Sandy clay	Sandy clay	Sandy clay	Sandy clay

TABLE V  
 PARTICLE SIZE DISTRIBUTION: MAKONA V SOIL  
 SAMPLES USED IN MINERAL ANALYSIS

Sample No.	16	17 & 18	19 & 20
Depth Cm.	0 - 12	12 - 47	47 - 140
% Sand	18	12	10
% Silt	16	10	12
% Clay	66	78	78
Textural class	Clay	Clay	Clay

TABLE VI  
 PARTICLE SIZE DISTRIBUTION: KONJO VI SOIL  
 SAMPLE USED IN MINERAL ANALYSIS

Sample No.	21 & 22	24 & 25
Depth Cm.	0 - 37	68 - 123
% Sand	20	50
% Silt	16	16
% Clay	64	34
Textural class	Clay (very fine)	Sandy clay loam

TABLE VII  
 PARTICLE SIZE DISTRIBUTION: N'GISI KONJA VII SOIL  
 SAMPLE USED IN MINERAL ANALYSIS

Sample No.	26 & 27	28
Depth Cm.	0 - 37	37 - 80
% Sand	20	18
% Silt	10	16
% Clay	70	66
Textural class	Clay (very fine)	Clay (very fine)

TABLE VIII

PARTICLE SIZE DISTRIBUTION: RED WELEDU VIII SOIL  
 SAMPLES USED IN MINERAL ANALYSIS

Sample No.	29	31 & 32
Depth Cm.	0 - 15	62 - 160
% Sand	36	26
% Silt	16	20
% Clay	48	54
Textural class	Sandy clay	Clay (fine)

TABLE IX

PARTICLE SIZE DISTRIBUTION: RED WELEDU/STONES IX SOIL  
 SAMPLES USED IN MINERAL ANALYSIS

Sample No.	33 & 34	35 & 36
Depth Cm.	0 - 47	47 - 124
% Sand	40	18
% Silt	18	32
% Clay	42	50
Textural class	Sandy clay	Clay (fine)



TABLE X  
PARTICLE SIZE DISTRIBUTION: YELLOW WELEDU X SOIL  
SAMPLES USED IN MINERAL ANALYSIS

Sample No.	37 & 38	39 & 40
Depth Cm.	0 - 36	36 - 125
% Sand	56	42
% Silt	12	8
% Clay	32	50
Textural class	Sandy clay loam	Clay (fine)

these soils especially in the lower layers of the soil profile is a diagnostic feature of these soils as has previously been reported (18). Low silt content is also characteristic of the red and yellow soils of the tropics and subtropics (15).

#### Chemical Properties of the Soils

The chemical properties of the soils that have been studied are reported in Tables XI - XIX. These data show that these soils are acid soils with acidity ranging from weakly acid to strongly acid. The pH in water (1:1) for all profiles ranges from weakly acid of pH 6.6 to strongly acid pH 4.5. A pH reading of 1 N KCl reveals these pH's to fall within the range of 3.9 to 5.6. This drop in pH is due to a decrease in the diffuse double layer thickness of the clay particles of the soil when the potassium salt solution was added as reported by Bear (13) and Russell (83). According to these authors, for unsaturated clay particles in an aqueous suspension, the number of hydronium ions dissociating from the diffuse double layer into the soil solution is inversely proportional to the thickness of the layer. Addition of an electrolyte decreases the thickness of the layer and brings about a replacement of the exchangeable hydronium ions from the clay by the electrolyte cations. The replaced hydronium ions then increase the acidity of the solution. The pH of an acid or slightly acid clay is thus lowered by the addition of a salt.

All of these soils are found to be more acid at the surface than at the subsurface layers. The Red Weledu soil does not exhibit appreciable differences between the acidity of its lower and upper layer. A look at the mean averages given in Table XX indicates that

TABLE XI  
CHEMICAL CHARACTERISTICS OF THE COMASADU I SOIL

Determination	Depth cm Sample No.	0 - 10 1	10 - 20 2	20 - 50 3	50 - 90 4	90 - 140 5
pH in H <sub>2</sub> O	(1:1)	5.1	5.1	5.4	5.5	5.8
pH in 1N KCl	(1:1)	4.5	4.5	4.5	4.5	4.7
CEC* (m.eq./100 gm)		6.76	4.17	3.70	4.30	4.01
Exchangeable cations (m.e./100 gm)						
Calcium		2.20	1.09	0.90	1.20	1.22
Magnesium		1.65	0.82	0.33	0.26	0.28
Potassium		0.21	0.18	0.11	0.11	0.11
Sodium		0.94	0.45	0.49	0.44	0.48
Manganese		0.11	0.07	0.08	0.06	0.07
Copper		0.13	0.10	0.05	0.05	0.05
Iron		0.14	0.09	0.09	0.14	0.09
Zinc		0.12	0.02	0.03	0.02	0.04
% Base Saturation		67.06	61.10	49.38	44.16	52.09
Exchangeable Acidity** (A <sup>+</sup> 3 + H <sup>+</sup> )		29.50	25.34	21.19	21.19	13.76
Total Phosphorus (PPM)		39.20	103.50	11.52	131.10	12.36
Available Phosphorus (PPM)		1.16	1.09	1.24	19.00	7.00
Organic Phosphorus (PPM)		14.70	21.60	28.70	30.72	23.30
% Total Nitrogen		0.03	0.03	0.06	0.07	0.04
% Organic Matter		4.18	2.80	1.68	0.93	0.86
% Organic Carbon		2.43	1.62	0.98	0.54	0.50
Carbon:Nitrogen Ratio		68.43	48.83	16.85	7.00	12.00

\*Cation Exchange Capacity (m.e./100 grams).

\*\*In milliequivalents per 100 grams.

TABLE XII  
CHEMICAL CHARACTERISTICS OF THE DALIN II  
AND FOYA MODEL III SOILS

	Depth cm	0 - 26	33 - 60	60 - 104	104 - 120
Determination	Sample No.	6	7	8	9
pH in H <sub>2</sub> O (1:1)		4.5	5.2	5.4	5.7
pH in 1N <sup>2</sup> KCl (1:1)		4.0	4.3	4.4	4.6
CEC* (m.eq./100 gm)		7.02	5.75	4.70	4.73
Exchangeable cations (m.e./100 gm)					
Calcium		0.30	1.36	1.50	1.22
Magnesium		0.20	1.18	0.69	0.49
Potassium		0.26	0.12	0.12	0.15
Sodium		0.48	0.45	0.26	0.26
Manganese		0.01	0.02	0.02	0.02
Copper		0.05	0.05	0.10	0.06
Iron		0.14	0.14	0.14	0.14
Zinc		0.03	0.05	0.03	0.02
% Base Saturation		17.52	53.79	54.60	31.27
Exchangeable Acidity**		25.15	10.69	9.21	7.92
Total Phosphorus (PPM)		9.08	16.28	13.64	11.22
Available Phosphorus (PPM)		1.26	8.30	1.38	0.18
Organic Phosphorus (PPM)		4.70	21.16	10.72	4.40
% Total Nitrogen		0.04	0.11	0.03	0.02
% Organic Matter		4.15	1.22	1.12	0.74
% Organic Carbon		2.41	0.71	0.65	0.43
Carbon:Nitrogen Ratio		55.06	6.38	21.63	18.65

\*Cation Exchange Capacity (m.e./100 grams)

\*\*In milliequivalents per 100 grams.

TABLE XIII  
CHEMICAL CHARACTERISTICS OF THE FOYA DEEP IV SOIL

Deter- mination	Depth cm Sample No	0-18 10	18-38 11	38-72 12	72-105 13	105-140 14	18-38 15
pH in H <sub>2</sub> O (1:1)		4.60	4.90	5.10	5.60	5.80	5.70
pH in 1 N KCl (1:1)		4.10	3.90	4.20	4.20	4.50	5.30
CEC* (m.e./100 grams)		5.89	3.70	3.26	2.32	2.27	4.41
Exchangeable Cations (m.e./100 grams)							
Calcium		0.62	0.42	0.42	0.24	0.24	7.68
Magnesium		0.26	0.17	0.17	0.10	0.13	1.97
Potassium		0.16	0.31	0.19	0.11	0.12	0.19
Sodium		0.26	0.26	0.44	0.17	0.17	0.27
Manganese		0.01	0.10	0.01	0.10	0.01	0.05
Copper		0.10	0.04	0.13	0.05	0.10	0.05
Iron		0.14	0.16	0.14	0.14	0.16	0.21
Zinc		0.03	0.03	0.04	0.01	0.01	0.02
% Base Saturation		22.19	31.14	37.21	26.20	29.21	229.42
Exchangeable Acidity **		13.46	10.49	9.90	9.50	5.54	5.34
Total Phosphorus (PPM)		6.16	7.26	8.38	8.38	0.80	11.72
Available Phos- phorus (PPM)		0.62	0.16	0.18	0.14	0.10	7.31
Organic Phos- phorus (PPM)		4.72	3.36	2.28	0.68	0.20	3.60
% Total Nitrogen		0.08	0.09	0.05	0.04	0.05	0.18
% Organic Matter		2.73	1.79	1.00	0.90	0.56	2.94
% Organic Carbon		1.59	1.04	0.59	0.52	0.32	1.71
Carbon:Nitrogen Ratio		19.38	11.20	12.44	11.89	6.00	9.28

\*Cation Exchange Capacity (meq/100 grams).

\*\*In milliequivalents per 100 grams.

TABLE XIV  
CHEMICAL CHARACTERISTICS OF THE MAKONA V SOIL

Determination	Depth cm Sample No.	0 - 12 16	12 - 30 17	30 - 47 18	47 - 87 19	87 - 140 20
pH in H <sub>2</sub> O	(1:1)	4.8	5.4	6.0	6.1	5.8
pH in 1 <sup>2</sup> N KCl	(1:1)	4.2	4.3	4.5	4.9	4.4
Cation Exchange Capacity (m.eq/100)		10.48	6.18	5.44	5.78	5.28
Exchangeable Cations (m.e./100 grams)						
Calcium		1.00	1.01	0.80	1.00	1.00
Magnesium		0.57	0.40	0.40	0.49	0.53
Potassium		0.31	0.16	0.11	0.11	0.11
Sodium		0.26	0.27	0.26	0.43	0.32
Manganese		0.11	0.05	0.06	0.11	0.02
Copper		0.06	0.05	0.05	0.05	0.05
Iron		0.21	0.16	0.16	0.16	0.21
Zinc		0.02	0.06	0.02	0.43	0.02
% Base Saturation		20.37	29.68	28.81	35.12	36.72
Exchangeable Acidity*		33.66	19.80	13.37	11.68	11.88
Total Phosphorus (PPM)		1.52	1.24	1.30	1.54	1.38
Available Phosphorus (PPM)		1.50	0.14	0.22	0.54	0.32
Organic Phosphorus (PPM)		2.56	1.36	1.60	3.92	3.18
% Total Nitrogen		0.17	0.03	0.03	0.03	0.01
% Organic Matter		4.12	1.45	1.71	0.66	0.79
% Organic Carbon		2.39	0.84	1.00	0.38	0.46
Carbon:Nitrogen Ratio		14.08	28.02	35.57	15.35	33.00

\*In Milliequivalents per 100 grams.

TABLE XV

## CHEMICAL CHARACTERISTICS OF THE KONJO VI SOIL

Determination	Depth cm. Sample No.	0 - 8 21	8 - 37 22	37 - 68 23	68 - 101 24	101 - 123 25
pH in H <sub>2</sub> O (1:1)		5.10	5.30	6.20	6.20	6.60
pH in 1 <sup>2</sup> N KCl (1:1)		4.60	4.60	5.20	5.50	5.30
Cation Exchange Capacity (m.e./100 gm)		6.39	5.36	2.70	1.77	1.58
Changeable Cations (m.e./100 grams)						
Calcium		0.90	0.40	0.68	0.56	0.50
Magnesium		0.53	0.13	0.17	0.17	0.10
Potassium		0.31	0.13	0.13	0.11	0.11
Sodium		0.32	0.25	0.44	0.30	0.67
Manganese		0.04	0.01	0.02	0.02	0.02
Copper		0.05	0.06	0.04	0.05	0.05
Iron		0.16	0.23	0.23	0.21	0.14
Zinc		0.02	0.02	0.02	0.02	0.01
% Base Saturation		32.16	12.20	52.30	64.97	61.77
Exchangeable Acidity*		14.26	11.68	10.89	8.91	8.71
Total Phosphorus (PPM)		2.27	1.32	1.20	1.40	1.44
Available Phosphorus (PPM)		0.35	0.22	0.08	0.24	0.32
Organic Phosphorus (PPM)		2.60	0.32	0.20	0.36	9.60
% Total Nitrogen		0.70	0.06	0.02	0.01	0.12
% Organic Matter		1.43	2.73	1.15	1.01	0.42
% Organic Carbon		0.83	1.59	0.67	0.58	0.25
Carbon:Nitrogen Ratio		11.88	28.39	33.34	41.77	2.05

\*In milliequivalents per 100 grams.

TABLE XVI

## CHEMICAL CHARACTERISTICS OF THE N'GISI KONJA VII SOIL

Determination	Depth cm.	0 - 10	10 - 37	37 - 80
	Sample No.	26	27	28
pH in H <sub>2</sub> O	(1:1)	4.80	4.80	4.80
pH in 1 <sup>N</sup> KCl	(1:1)	4.70	4.30	4.10
Cation Exchange Capacity (m.e./100 gm)		6.73	6.26	5.17
Exchangeable Cations (m.e./100 gms)				
Calcium		1.70	1.20	1.46
Magnesium		0.60	0.51	0.51
Potassium		0.31	0.15	0.15
Sodium		0.32	0.61	0.45
Manganese		0.47	0.02	0.02
Copper		0.05	0.13	0.05
Iron		0.28	0.23	0.25
Zinc		0.02	1.00	0.03
% Base Saturation		43.58	36.97	42.81
Exchangeable Acidity*		27.72	21.19	9.70
Total Phosphorus (PPM)		1.48	1.10	0.76
Available Phosphorus (PPM)		1.64	1.50	1.34
Organic Phosphorus (PPM)		26.16	19.96	12.08
% Total Nitrogen		0.13	0.11	0.05
% Organic Matter		3.69	3.68	0.96
% Organic Carbon		2.15	2.14	0.56
Carbon:Nitrogen Ratio		16.26	20.36	10.92

\*In milliequivalents per 100 grams.



TABLE XVII  
 CHEMICAL CHARACTERISTICS OF THE RED WELEDU VIII SOIL

Determination	Depth cm Sample No.	0 - 15 29	15 - 62 30	62 - 135 31	135 - 160 32
pH in H <sub>2</sub> O	(1:1)	5.00	5.50	6.20	5.70
pH in 1 <sup>N</sup> KCl	(1:1)	4.40	4.80	4.80	4.50
CEC* (m.e./100 gm)		5.33	3.00	3.90	3.00
Exchangeable cations (m.e./100 grams).					
Calcium		0.90	0.74	0.56	0.80
Magnesium		0.52	0.35	0.25	0.33
Potassium		0.31	0.18	0.18	0.31
Sodium		0.04	0.02	0.02	0.04
Copper		0.10	0.05	0.04	0.05
Iron		0.21	0.21	0.21	0.16
Zinc		0.01	0.03	0.02	0.09
% Base Saturation		36.75	53.30	28.87	59.40
Exchangeable Acidity**		12.67	11.09	10.49	8.32
Total Phosphorus (PPM)		1.06	1.02	0.88	0.90
Available Phosphorus (PPM)		0.68	0.04	0.04	0.04
Organic Phosphorus (PPM)		10.96	8.28	11.16	6.56
% Total Nitrogen		0.02	0.03	0.02	0.02
% Organic Matter		1.70	0.99	0.46	0.20
% Organic Carbon		0.99	0.58	0.27	0.12
Carbon:Nitrogen Ratio		61.66	22.13	12.62	8.47

\*Cation Exchange Capacity (meq/100 grams).

\*\*In milliequivalents per 100 grams.

TABLE XVIII  
 CHEMICAL CHARACTERISTICS OF THE RED  
 WELEDU/STONES IX SOIL

Determination	Depth cm. Sample No.	0 - 25 33	25 - 47 34	47 - 102 35	102 - 124 36
pH in H <sub>2</sub> O	(1:1)	6.10	5.50	5.90	6.20
pH in 1 <sup>2</sup> N KCl	(1:1)	5.60	4.60	5.00	4.80
Cation Exchange Capacity (m.e./100 gm)		11.93	6.10	5.20	5.36
Exchangeable Cations (m.e./100 grams)					
Calcium		7.25	2.14	2.99	1.97
Magnesium		2.30	1.15	0.98	0.59
Potassium		0.23	0.23	0.31	0.18
Sodium		0.35	0.26	0.57	0.48
Manganese		0.06	0.06	0.07	0.02
Copper		0.03	0.04	0.04	0.04
Iron		0.16	0.21	0.21	0.21
Zinc		0.02	0.01	0.07	0.07
% Base Saturation		84.85	42.98	91.60	60.07
Exchangeable Acidity*		15.44	16.24	8.71	5.94
Total Phosphorus (PPM)		1.48	1.75	1.30	1.26
Available Phosphorus (PPM)		0.71	0.77	0.12	0.08
Organic Phosphorus (PPM)		8.16	9.84	3.04	21.52
% Total Nitrogen		0.04	0.03	0.01	0.02
% Organic Matter		3.44	2.04	0.38	0.17
% Organic Carbon		0.27	1.19	0.22	0.10
Carbon:Nitrogen Ratio		7.31	37.12	27.39	5.58

\*In milliequivalents per 100 grams.

TABLE XIX  
CHEMICAL CHARACTERISTICS OF THE YELLOW WELEDU X SOIL

Determination	Depth cm Sample No.	0 - 22 37	22 - 36 38	36 - 74 39	74 - 125 40
pH in H <sub>2</sub> O (1:1)		4.60	4.90	5.00	6.00
pH in 1 <sup>2</sup> N KCl (1:1)		4.10	4.20	4.40	4.40
CEC (m.e./100 gm)		4.83	4.07	3.56	2.96
Exchangeable Cations (m.e./100)					
Calcium		0.73	0.56	0.46	0.30
Magnesium		0.33	0.21	0.21	0.17
Potassium		0.20	0.18	0.16	0.16
Sodium		0.44	0.43	0.27	0.41
Manganese		0.02	0.02	0.02	0.02
Copper		0.04	0.04	0.04	0.04
Iron		0.21	0.21	0.21	0.21
Zinc		0.01	0.02	0.01	0.02
% Base Saturation		35.18	33.98	31.00	35.27
Exchangeable Acidity*		11.78	3.76	7.92	9.11
Total Phosphorus (PPM)		1.04	1.10	0.96	1.02
Available Phosphorus (PPM)		0.62	0.38	0.21	0.08
Organic Phosphorus (PPM)		1.44	0.22	0.20	0.60
% Total Nitrogen		0.14	0.01	0.05	0.02
% Organic Matter		2.04	1.26	0.86	0.55
% Organic Carbon		1.19	0.73	0.50	0.32
Carbon:Nitrogen Ratio		8.48	146.16	10.92	19.98

\*In milliequivalents per 100 grams.

TABLE XX

MEAN AVERAGE CHEMICAL CHARACTERISTICS OF EACH  
SERIES OF SOIL (I-X)

Series	I	II	III	IV	V	VI	VII	VIII	IX	X
pH in water (1:1)	5.38	4.50	5.43	5.28	5.62	5.88	4.80	5.60	5.93	5.13
pH in 1N KCl (1:1)	4.54	4.00	4.43	4.37	4.46	5.04	4.37	4.62	5.00	4.28
CEC (m.e./100 gm)	4.59	7.02	5.06	3.64	6.63	3.56	6.05	4.18	7.15	3.86
Exchangeable cations (m.e./100 grams)										
Calcium	1.32	0.32	1.36	1.60	0.96	0.61	1.45	0.75	3.59	0.51
Magnesium	0.67	0.20	0.79	0.47	0.48	0.22	0.54	0.36	1.23	0.23
Potassium	0.14	0.26	0.13	0.18	0.16	0.22	0.20	0.24	0.24	0.18
Sodium	0.47	0.48	0.32	0.26	0.31	0.40	0.46	0.30	0.42	0.39
Manganese	0.08	0.01	0.02	0.02	0.07	0.04	0.17	0.03	0.05	0.02
Copper	0.08	0.05	0.07	0.08	0.05	0.05	0.08	0.06	0.04	0.04
Iron	0.11	0.14	0.14	0.16	0.18	0.19	0.25	0.19	0.20	0.21
Zinc	0.05	0.03	0.03	0.02	0.11	0.02	0.35	0.03	0.04	0.02
% Base Saturation	54.75	17.52	46.55	62.63	30.14	31.69	41.12	44.58	69.88	33.86
Exchangeable Acidity*	22.20	25.15	9.27	7.00	15.40	10.89	19.54	10.64	11.58	8.14
Total Phosphorus (PPM)	59.54	9.08	13.71	7.12	1.40	1.53	1.11	0.97	1.45	1.03
Available Phosphorus (PPM)	2.10	1.26	3.29	1.42	0.54	0.24	0.99	0.20	0.42	0.32
Organic Phosphorus (PPM)	19.48	4.70	12.09	2.47	2.52	2.61	19.40	9.24	10.64	0.62
% Total Nitrogen	0.05	0.04	0.05	0.08	0.05	0.06	0.10	0.02	0.03	0.06
% Organic Matter	2.09	4.15	1.03	1.65	1.75	1.35	2.78	0.84	1.51	1.18
% Carbon (Organic)	1.21	2.41	0.60	0.96	1.01	0.78	1.62	0.49	0.45	0.69
C:N Ratio	20.86	55.06	15.55	8.47	25.20	23.49	15.85	26.22	19.35	46.39

\*m.e./100 grams.

the N'gisi Konjo and the Comasadu soils are the most acid. The Makona, Konjo, Red Weledu, and Red Weledu (with stones) soils are slightly acid. The exchangeable acidity ( $Al^{+3} + H_3^{+}O$ ) for all samples ranges from 3.76 m.e./100 grams in the Yellow Weledu soil to 33.66 m.e./100 grams in the Makona soils. Table XX shows that the exchangeable acidities for all soils average quite high. This means that a larger percentage of their total exchange capacities is due to both hydronium and aluminum ions. With the exception of the Dalin soils, the Comasadu soil had the highest average exchangeable acid value and the N'gisi Konjo soil ranked second. These soils like many other tropical soils are very acid.

The cation exchange capacity is very low for all samples. The lowest (1.58 m.e./100 grams) is for the 123 cm. depth of the Kanjo soil. The highest (11.93 m.e./100 grams) is for the 25 cm. depth of the Red Weledu/Stones soil. All of these soils exhibit a lower CEC at depth than at the surface. The base status of these soils is higher at the surface than at depth despite leaching of bases down the profile by rain water as shown in Tables XI - XIX. Foth and Turk (37) and Bennema (15) explained that the roots of higher plants absorb nutrient elements from deep into the soil solum and transport them through the stems to the surface by falling leaves, dead debris and plant root exudates. The process of leaching is probably responsible for the irregular accumulation of bases at points down the profile in these soils. This results in a higher or lower value for CEC and bases at some points than at other points near the surface or deep below the surface in the profile. This phenomenon is demonstrated by many of the soils in this study. On the average, the Red Weledu/Stone has the

highest cation exchange capacity (CEC) value (7.15 m.eq./100 gm). The Makana and N'gisi soils are second in value of CEC, 6.63 and 6.05, respectively. The Dalin soil at one depth in the profile had a cation exchange capacity of 7.02 m.e./100 grams. It is not possible to compare it with other soils in this study because it was represented by only one sample. The remaining six soils had a average CEC below eight milliequivalents per 100 grams of soil. The Konjo soil which is one of the medium acid soils of Liberia had the lowest average CEC (3.56 m.e./100 grams).

With respect to the exchangeable bases, calcium content was the highest in all soils as expected. Red Weledu/Stone had the highest calcium saturation among these soils. Magnesium saturation was second to calcium in all soils. Sodium values in all soils was next to magnesium.

The low percent base saturation of these soils is characteristic of the red and yellow soils referred to as tropical Ultisols. Some workers (17) have indicated that the dark surface of these soils, classified as the umbric epipedon under natural conditions normally has a base saturation of less than 50% and that a diagnostic depth for determining base saturation should be set at 125 cm (50 in.) or 180 cm (72 in.) from the surface and must have a base saturation for the subsoil of less than 35%. Most of the profiles for the soils studied have depths less than 125 cm. The base saturation of these soils conforms well with the above restrictions. Few of these soils, however, have base saturation greater than 50% for the surface and greater than 35% for the 125th cm. depth. These high base saturation percentages could probably be due to factors such as accumulation of bases to a particular depth caused by leaching, method of collecting

the samples, and laboratory errors.

The micronutrient element status of these soils is very low. Of the four trace elements studied, manganese, iron, zinc, and copper, all but copper in some cases, have values falling below 1 ppm. Baker and Tucker (7) have cited 1.0+ ppm of zinc, 4.5 + ppm of iron and 1.0 + ppm manganese to be adequate for growing crops. They also recommend 10.0 + ppm of iron as adequate for lawns.

All three forms of phosphorus: total phosphorus, available phosphorus, and organic phosphorus were found to be very low for all samples examined. The Camasadu soil however, appears to have more total phosphorus than the other soils. As can be seen from Tables XI-XIX and XX a greater amount of this total phosphorus is in the organic form. Data reported in Table XX show an average total phosphorus content of Camasadu soil to be 59.54 ppm of this amount, 32.72 percent was in the organic form while only 3.52 percent was in the available form as explained earlier (39,57,67,74,83). The difference in phosphorus content of 63.76 percent is probably in other inorganic forms not easily available to plants, perhaps due to fixation by iron and aluminum oxides which dominates these soils. The Foya Model soil has the second highest content of total phosphorus both on an individual sample basis and on a total average basis and it had a total average phosphorus content of 13.71 ppm. Unlike the Camasadu soil, 24 percent of the phosphorus in the Foya Model soil was in the available form. The remaining 76 percent was in the organic and other inorganic forms not readily soluble for plant growth. It can be observed from the data in Tables XI-XIX and XX that in some samples, the amount of organic phosphorus extracted was higher than the

value for total phosphorus for the same sample. This is due to differences in the methods of extraction.

The percent total nitrogen is very low for all soils, but the percent organic matter is high in these soils. As indicated by some authors (93) both nitrogen and organic matter content are higher in the surface layer than in the lower layers of the profile. On an average basis, the N'gisi soil has the highest percentage of both organic matter and total nitrogen. The percent organic carbon is also high for these soils corresponding to the high organic matter content. The carbon:nitrogen ratio for some of these soils for example Comasadu, Dalin, and Red Weledu is too high especially at the surface and should retard mineralization as discussed by Tisdale and Nelson (93). The C:N ratio decreased with depth. Other soils: Foya Model, N'gisi, Konja, and Yellow Weledu have a C:N ratio adequately low to permit mineralization of nitrogen. For some soils, for example Konjo, neither mineralization nor immobilization can be expected.

The data presented on these soils can be said to be in agreement with those reported by Reed (81) and other investigators (104). Results of a recent chemical determination on some Liberian soils are given in the Appendix.

#### Nutrient Element Requirements

The results of the tests conducted for predicting the amount of nutrient elements as fertilizers required for optimum crop production as introduced by Baker (5,6) are given in Table XXI. Sulfur was not included in this study and no results are reported for phosphorus. All of the soils studied were very efficient in removal of the nutrient



TABLE XXI

SOIL CHARACTERISTICS OF NUTRIENT ELEMENTS  
REQUIREMENTS (BAKER'S PROCEDURE)

Nos.	Soil Sample	Profile cm	Nutrient Elements (m.e./100 grams)						
			Ca	Mg	K	Fe	Mn	Cu	Zn
1	Comasadu	0-10	0.99	0.64	0.67	0.26	0.02	0.00	0.01
2		10-20	1.44	0.16	-0.03	0.13	0.02	0.00	0.01
3		20-50	1.51	-0.10	-0.01	-0.01	0.02	0.00	-0.01
4		50-90	1.80	-0.12	-0.01	-0.01	0.01	0.00	-0.01
5		90-140	1.64	-0.12	-0.01	-0.06	0.02	0.00	-0.01
6		0-26	1.74	-0.04	0.13	0.58	0.01	0.00	-0.01
7	Foya Model	33-60	0.58	0.12	-0.01	0.14	0.01	0.00	-0.01
8		60-104	0.74	0.33	-0.01	0.26	-0.02	0.00	-0.01
9		104-120	1.53	-0.08	-0.01	0.16	-0.02	0.00	-0.01
10	Foya Deep	0-18	1.31	0.00	0.19	0.22	-0.02	0.00	-0.01
11		18-38	1.29	-0.01	0.10	0.10	-0.02	0.00	-0.01
12		38-72	0.93	0.00	-0.04	-0.01	-0.02	0.00	-0.01
13		72-105	1.12	-0.15	-0.02	-0.02	-0.02	0.00	-0.01
14		105-140	0.69	-0.16	-0.03	-0.02	-0.02	0.00	-0.01
15		18-38	0.72	0.06	-0.03	0.44	0	0.00	-0.01
16	Makana	0-12	0.84	0.12	0.10	0.03	0.04	0.00	-0.01
17		12-30	0.76	-0.06	0.07	0.02	0.02	0.00	-0.01
18		30-47	0.93	-0.04	-0.01	-0.06	0.01	0.00	-0.01
19		47-87	0.63	-0.06	-0.01	-0.03	0.02	0.00	-0.01
20		87-140	0.71	-0.08	-0.01	-0.03	-0.02	0.00	-0.01
21	Kanjo	0-8	0.73	0	0.10	0.49	0.01	0.00	-0.01
22		8-37	0.12	-0.15	-0.03	0.22	0	0.00	-0.01
23		37-68	1.17	-0.16	-0.02	-0.01	-0.02	0.00	-0.01
24		68-101	0.75	-0.18	-0.01	-0.01	-0.02	0.00	-0.01
25		101-123	0.73	-0.24	-0.01	0.03	-0.02	0.00	-0.01
26	N'gisi Konja	0-10	0.97	0.07	0.10	0.08	0	0.00	-0.01
27		10-37	-0.05	0.07	0	0.19	0	0.00	-0.01
28		37-80	0.51	0.45	0	0.10	0	0.00	-0.01
29	Red Weledu	0-15	1.18	0.01	0.10	0.10	0	0.00	-0.01
30		15-62	0.60	0.04	0.02	0.08	0	0.00	-0.01
31		62-135	0.45	-0.09	0.01	0.03	-0.02	0.00	-0.01
32		135-160	0.88	-0.03	0.12	0.09	-0.02	0.00	-0.01
33	Red Weledu/Stones	0-25	0.68	0.47	0.01	0.06	0.02	0.00	-0.01
34		25-47	1.63	0.35	0	0.02	-0.02	0.00	-0.01
35		47-102	0.83	0.16	-0.01	-0.06	0.02	0.00	-0.01
36		102-124	1.42	0	0.03	-0.06	-0.02	0.00	-0.01

TABLE XXI "CONTINUED"

Nos.	Soil Sample	Profile cm	Nutrient Elements (m.e./100 grams)						
			Ca	Mg	K	Fe	Mn	Cu	Zn
37	Yellow Weledu	0-22	0.83	0.02	0.08	0.02	0	0.00	-0.01
38		22-36	0.99	0.12	0.06	0	0	0.00	-0.01
39		36-74	1.14	-0.13	0.05	-0.03	-0.02	0.00	-0.01
40		74-125	0.62	-0.17	0.01	-0.03	-0.02	0.00	-0.01

Note: Bakers chemical refers to nutrient elements that have been analyzed by Baker's procedure (Table V).

elements added to the extracting solution. In general, it can be said that these soils are very deficient in these elements. These soils will therefore respond to an application of fertilizers having these elements. The major essential elements, magnesium and potassium are the more deficient for all soils as shown in Table XXI. Although crop growing will respond to calcium application, less calcium was removed from the extracting solution as compared to other elements. All trace elements were found to be very deficient in these soils. Results shown in this study indicate that a considerable amount of these elements were removed by all soils. Removal of these elements could be due to efficient adsorption by the soil and the determination or detection limit of the atomic absorption spectrophotometer was exceeded and no value was reported, for example, for copper. Addition of these elements in a fertilizer program for the soils studied would probably be beneficial. Although, the test indicates that these soils will respond to iron in a fertilizer, care must be taken as to the amount of iron to add to a fertilizer for these soils. It has been pointed out that these soils contain ironstone in their subsurface layer and perhaps free iron oxide also.

Correlation coefficients were determined on all of the chemical analyses reported on these soils. It is not practicable or necessary to report every result in this paper, therefore, those that were significant and also those that were worth mentioning are reported in Tables XXII through XXVI and XXVII through XXXVII. Correlations shown in Tables XXII through XXVI that are due to soil factors and data shown in Tables XXVII through XXXVII showed correlations where soil effects have been removed or not considered.

TABLE XXII

CORRELATION COEFFICIENTS DUE TO SOIL FACTOR: TOTAL  
PHOSPHORUS (PPM) VERSUS OTHER FRACTIONS

Other Fractions	Total Phosphorus	Remarks
Available Phosphorus (PPM)	0.96**	Significant at 1% level
Organic Phosphorus (PPM)	0.75*	Significant at 5% level
Organic Matter	0.73*	Significant at 5% level
% Total Nitrogen	-0.10	Not significant
Carbon:Nitrogen Ratio	0.28	Not significant
Baker's Calcium	0.67*	Significant at 5% level
Baker's Magnesium	0.06	Not significant
Baker's Potassium	-0.33	Not significant
Baker's Manganese	0.61	Not significant
Exchangeable Calcium	0.01	Not significant
Exchangeable Magnesium	-0.45	Not significant
Exchangeable Manganese	0.59	Not significant
Exchangeable Potassium	-0.45	Not significant

TABLE XXIII

CORRELATION COEFFICIENTS DUE TO SOIL FACTORS: AVAILABLE  
P (PPM) VERSUS OTHER FRACTIONS

Other Fractions	Available Phosphorus	Remarks
Organic Phosphorus (PPM)	0.78**	Significant at 1% level
Organic Matter	0.71*	Significant at 5% level
% Total Nitrogen	0.07	Not significant
Carbon:Nitrogen Ratio	0.11	Not significant
Baker's Calcium	0.61	Not significant
Baker's Magnesium	0.37	Not significant
Baker's Potassium	0.37	Not significant
Baker's Manganese	0.57	Not significant
Exchangeable Calcium	0.05	Not significant
Exchangeable Magnesium	0.28	Not significant
Exchangeable Potassium	-0.52	Not significant
Exchangeable Manganese	0.51	Not significant

TABLE XXIV

CORRELATION COEFFICIENTS DUE TO SOIL FACTORS: ORGANIC  
MATTER VERSUS OTHER FRACTIONS

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Other Fractions	Organic Matter	Remarks
% Total Nitrogen	0.28	Not significant
Carbon:Nitrogen Ratio	0.40	Not significant
Baker's Calcium	0.52	Not significant
Baker's Magnesium	0.12	Not significant
Baker's Potassium	0.11	Not significant
Baker's Manganese	0.66*	Significant at 5% level
Exchangeable Calcium	0.03	Not significant
Exchangeable Magnesium	0.08	Not significant
Exchangeable Sodium	0.72*	Significant at 5% level

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TABLE XXV

CORRELATION COEFFICIENTS DUE TO SOIL FACTORS: ORGANIC  
P (PPM) VERSUS OTHER FRACTIONS

Other Fractions	Organic Phosphorus	Remarks
Organic Matter	0.66*	Significant at 5% level
% Total Nitrogen	-0.09	Not significant
Baker's Calcium	0.27	Not significant
Baker's Magnesium	0.65*	Significant at 5% level
Baker's Potassium	-0.50	Not significant
Baker's Manganese	0.57	Not significant
Exchangeable Calcium	0.28	Not significant
Exchangeable Sodium	0.73	Significant at 5% level
Carbon:Nitrogen Ratio	0.26	Not significant

TABLE XXVI

OTHER CORRELATION COEFFICIENTS THAT ARE DUE TO SOIL  
FACTORS AND ARE SIGNIFICANT

	r	Remarks
Baker's Mg Versus Baker's K	-0.71	Significant at 5% level
Baker's Mg Versus Exchange Ca	0.73	Significant at 5% level
Baker's Mg Versus Exchange Mg	0.86	Significant at 1% level
Baker's Mn Versus Exchange Mn	0.88	Significant at 1% level
Exchange Ca Versus Baker's Mg	0.92	Significant at 1% level
Exchange Mg Versus Baker's Mn	0.96	Significant at 1% level



TABLE XXVII

SIGNIFICANT CORRELATION COEFFICIENTS: SOIL EFFECTS REMOVED  
TOTAL PHOSPHORUS VERSUS OTHER FRACTIONS

	r	Remarks
Available Phosphorus (PPM)	0.50	Significant at 1% level
Organic Phosphorus (PPM)	0.43	Significant at 5% level
Organic Matter	-0.42	Significant at 5% level
% Total Nitrogen	0.80	Significant at 1% level
Baker's Calcium	0.59	Significant at 1% level
Baker's Magnesium	0.77	Significant at 1% level
Baker's Potassium	0.99	Significant at 1% level
Baker's Iron	0.87	Significant at 1% level
Baker's Manganese	0.66	Significant at 1% level
Exchangeable Calcium	0.82	Significant at 1% level
Exchangeable Magnesium	0.82	Significant at 1% level
Exchangeable Potassium	0.84	Significant at 1% level
Exchangeable Sodium	0.71	Significant at 1% level
Exchangeable Copper	0.85	Significant at 1% level
Exchangeable Iron	0.45	Significant at 1% level
Exchangeable Zinc	0.82	Significant at 1% level

TABLE XXVIII

SIGNIFICANT CORRELATION COEFFICIENTS: SOIL EFFECTS REMOVED  
AVAILABLE PHOSPHORUS (PPM) VERSUS OTHER FRACTIONS

	r	Remarks
Organic Phosphorus (PPM)	0.435	Significant at 5% level
Organic Matter	0.936	Significant at 1% level
% Total Nitrogen	0.408	Significant at 5% level
Baker's Calcium	0.693	Significant at 1% level
Baker's Potassium	0.409	Significant at 5% level
Baker's Iron	0.825	Significant at 1% level
Baker's Manganese	0.623	Significant at 1% level
Exchangeable Magnesium	0.535	Significant at 1% level
Exchangeable Potassium	0.654	Significant at 1% level
Exchangeable Sodium	0.898	Significant at 1% level
Exchangeable Manganese	0.760	Significant at 1% level
Exchangeable Zinc	0.875	Significant at 1% level

TABLE XXIX  
ORGANIC PHOSPHORUS (PPM) VERSUS OTHER FRACTIONS

	r	Remarks
Organic Matter	0.614	Significant at 1% level
% Total Nitrogen	0.441	Significant at 5% level
Baker's Magnesium	-0.531	Significant at 1% level
Baker's Potassium	0.656	Significant at 1% level
Baker's Iron	0.699	Significant at 1% level
Baker's Manganese	0.501	Significant at 1% level
Exchangeable Calcium	0.613	Significant at 1% level
Exchangeable Magnesium	0.485	Significant at 1% level
Exchangeable Potassium	0.505	Significant at 1% level
Exchangeable Sodium	0.923	Significant at 1% level
Exchangeable Iron	0.828	Significant at 1% level
Exchangeable Zinc	0.944	Significant at 1% level

TABLE XXX  
SIGNIFICANT CORRELATION COEFFICIENTS: SOIL EFFECTS REMOVED  
BAKER'S CALCIUM VERSUS OTHER FRACTIONS

	r	Remarks
Baker's Manganese	-0.484	Significant at 1% level
Exchangeable Magnesium	-0.394	Significant at 5% level
Exchangeable Potassium	-0.553	Significant at 1% level
Exchangeable Sodium	-0.427	Significant at 5% level
Exchangeable Iron	0.427	Significant at 5% level
Exchangeable Zinc	0.499	Significant at 1% level

TABLE XXXI  
BAKER'S MAGNESIUM VERSUS OTHER FRACTIONS

	r	Remarks
Baker's Iron	0.563	Significant at 1% level
Baker's Manganese	0.392	Significant at 5% level
Exchangeable Calcium	0.406	Significant at 5% level
Exchangeable Magnesium	0.643	Significant at 1% level
Exchangeable Sodium	0.590	Significant at 1% level
Exchangeable Manganese	0.433	Significant at 5% level
Exchangeable Iron	0.534	Significant at 1% level
Exchangeable Zinc	0.670	Significant at 1% level

TABLE XXXII

## BAKER'S POTASSIUM VERSUS OTHER FRACTIONS

	r	Remarks
Baker's Iron	0.542	Significant at 1% level
Baker's Manganese	0.585	Significant at 1% level
Exchangeable Calcium	0.833	Significant at 1% level
Exchangeable Magnesium	0.372	Significant at 5% level
Exchangeable Iron	0.777	Significant at 1% level

TABLE XXXIII

SIGNIFICANT CORRELATION COEFFICIENTS: SOIL EFFECTS REMOVED  
ORGANIC MATTER VERSUS OTHER FRACTIONS

	r	Remarks
Baker's Calcium	0.504	Significant at 1% level
Baker's Iron	0.384	Significant at 5% level
Baker's Manganese	0.387	Significant at 5% level
Exchangeable Magnesium	0.358	Significant at 5% level
Exchangeable Sodium	0.452	Significant at 1% level
Exchangeable Copper	0.692	Significant at 1% level
Exchangeable Iron	0.785	Significant at 1% level
Exchangeable Zinc	0.759	Significant at 1% level

TABLE XXXIV

## % TOTAL NITROGEN VERSUS OTHER FRACTIONS

Tests	r	Remarks
Baker's Calcium	0.644	Significant at 1% level
Baker's Magnesium	0.819	Significant at 1% level
Baker's Iron	0.375	Significant at 1% level
Baker's Manganese	0.421	Significant at 5% level
Exchangeable Calcium	0.405	Significant at 5% level
Exchangeable Magnesium	0.399	Significant at 5% level
Exchangeable Potassium	0.357	Significant at 5% level
Exchangeable Sodium	0.427	Significant at 5% level
Exchangeable Iron	0.427	Significant at 5% level
Exchangeable Zinc	0.499	Significant at 1% level

TABLE XXXV

SIGNIFICANT CORRELATION COEFFICIENTS: SOIL EFFECTS REMOVED  
EXCHANGEABLE CALCIUM VERSUS OTHER FRACTIONS

	r	Remarks
Exchangeable Magnesium	0.868	Significant at 1% level
Exchangeable Potassium	0.549	Significant at 1% level
Exchangeable Sodium	0.823	Significant at 1% level
Exchangeable Manganese	0.374	Significant at 5% level
Exchangeable Copper	0.384	Significant at 5% level
Exchangeable Zinc	0.865	Significant at 1% level

TABLE XXXVI  
EXCHANGEABLE MAGNESIUM VERSUS OTHER FRACTIONS

Tests	r	Remarks
Exchangeable Sodium	0.808	Significant at 1% level
Exchangeable Manganese	0.482	Significant at 1% level
Exchangeable Copper	0.595	Significant at 1% level
Exchangeable Zinc	0.746	Significant at 1% level

TABLE XXXVII  
EXCHANGEABLE POTASSIUM VERSUS OTHER FRACTIONS

	r	Remarks
Exchangeable Sodium	0.798	Significant at 1% level
Exchangeable Manganese	0.537	Significant at 1% level
Exchangeable Copper	0.747	Significant at 1% level
Exchangeable Iron	0.641	Significant at 1% level

Data reported in Tables XXII through XXVI show a significant correlation between total phosphorus and available phosphorus, organic phosphorus, organic matter, and Baker's calcium\*. Higher correlations ( $r = 0.96$ ) and ( $r = 0.50$ ) seem to exist between total phosphorus and available phosphorus both with and without soil effects though earlier data revealed that a greater percentage of the total phosphorus in these soils is in the organic form. When soil effects are removed, total phosphorus correlates significantly well with other tests (i.e. % total nitrogen; Baker's calcium, magnesium, potassium, iron; exchangeable calcium, magnesium, potassium; and both organic and available phosphorus). Data reported in Table VII shows that as the amount of total phosphorus increased, the percent organic matter decreased. The data reported in Table XXIII shows that as the amount of available phosphorus is increased only the amount of organic phosphorus and percent organic matter correspondingly increase. But with the removal of soil factors, available phosphorus tends to correlate significantly with other tests like percent total nitrogen, Baker's calcium, potassium, iron and manganese. Available phosphorus also correlates significantly with the exchangeable cations including the trace elements. When soil effects are removed statistically, a negative correlation is found to exist between available phosphorus and Baker's magnesium. Organic phosphorus was found to correlate significantly with organic matter and Baker's magnesium. Organic phosphorus was also highly correlated with the rest of Baker's test parameters and the exchangeable cations including the trace elements.

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\* Calcium determined by Baker's Procedure.



Correlation between organic phosphorus and percent total nitrogen when soil effects are removed was significant at the 5 percent level.

When soil factors are considered both Baker's manganese and exchangeable sodium increase along with an increase in the organic matter content of all soils. Baker's calcium increased with an increase in organic matter content when soil effects are removed. Baker's iron and manganese also increased along with organic matter when soil factors are not considered. When soil effects are removed, correlation between organic matter and exchangeable magnesium, sodium, copper, iron, and zinc are all significant. Data reported in Table XXVI shows that Baker's magnesium has a negative correlation with Baker's potassium at the 5% level but a positive correlation with exchangeable calcium, magnesium and manganese at 1 percent level. Baker's manganese also was significantly correlated with exchangeable manganese.

Percent total nitrogen did not correlate significantly with any of the tests made when soil effects were taken into consideration. However, data reported in Table XXXIV shows that when soil factors are removed, percent total nitrogen correlates significantly with Baker's calcium, magnesium, iron, and manganese. The data in Table XXXIV also shows that exchangeable cations including the trace elements iron and zinc increase significantly with an increase in total nitrogen.

Data reported in Tables XXXV through XXXVII shows that exchangeable calcium correlates significantly well with other exchangeable cations. When the content of exchangeable magnesium increased, exchangeable sodium, manganese, copper and zinc also increased. An increase in exchangeable potassium was significantly correlated with

an increase in exchangeable sodium, manganese, copper, and iron.

#### Mineralogical Properties

X-ray diffraction patterns for the Comasadu soil are reported in Figure 1. When the fine clay fraction for the first 26 cm. depth (surface) was calcium saturated, it produced a 3.37A peak for quartz. The potassium saturated sample revealed a strong peak of 7.25A indicating the presence of kaolinite. Quartz was identified at 4.29A, 4.13A, 3.36A, and 3.32A. The second order of kaolinite peaks appeared at 3.57A and 3.62A. Heating of the potassium saturated sample at 500°C collapsed all of the kaolinite peaks after which quartz was identified at 3.36A and 4.13A. When the coarse fraction of this surface soil was calcium saturated it showed a kaolinite peak at 7.35A and quartz peaks at 4.11A and 3.37A. Potassium saturation produced a quartz peak at 3.36A which did not collapse upon heating. Clay mineral analysis of the subsurface (50-140 cm depth) of this soil gave results similar to that of the surface horizon. The calcium saturated sample of the fine clay fraction produced a broad and low intensity peak at 7.37A for metahalloysite of kaolinite. Potassium saturation of the sample resulted in a 3.36A peak for quartz. The kaolinite peak disappeared when the sample was heated to 500°C. The quartz peak was identified as a low intensity diffraction peak at 3.36A and 4.29A. The coarse clay fraction when calcium saturated produced kaolinite peaks at 7.43A and second order peak of kaolinite at 3.62A. Peaks for kaolinite and second order kaolinite were produced again at 7.31A and 3.59A, respectively. A high intensity quartz peak was identified at 3.36A. Heating of the sample to 500°C collapsed all

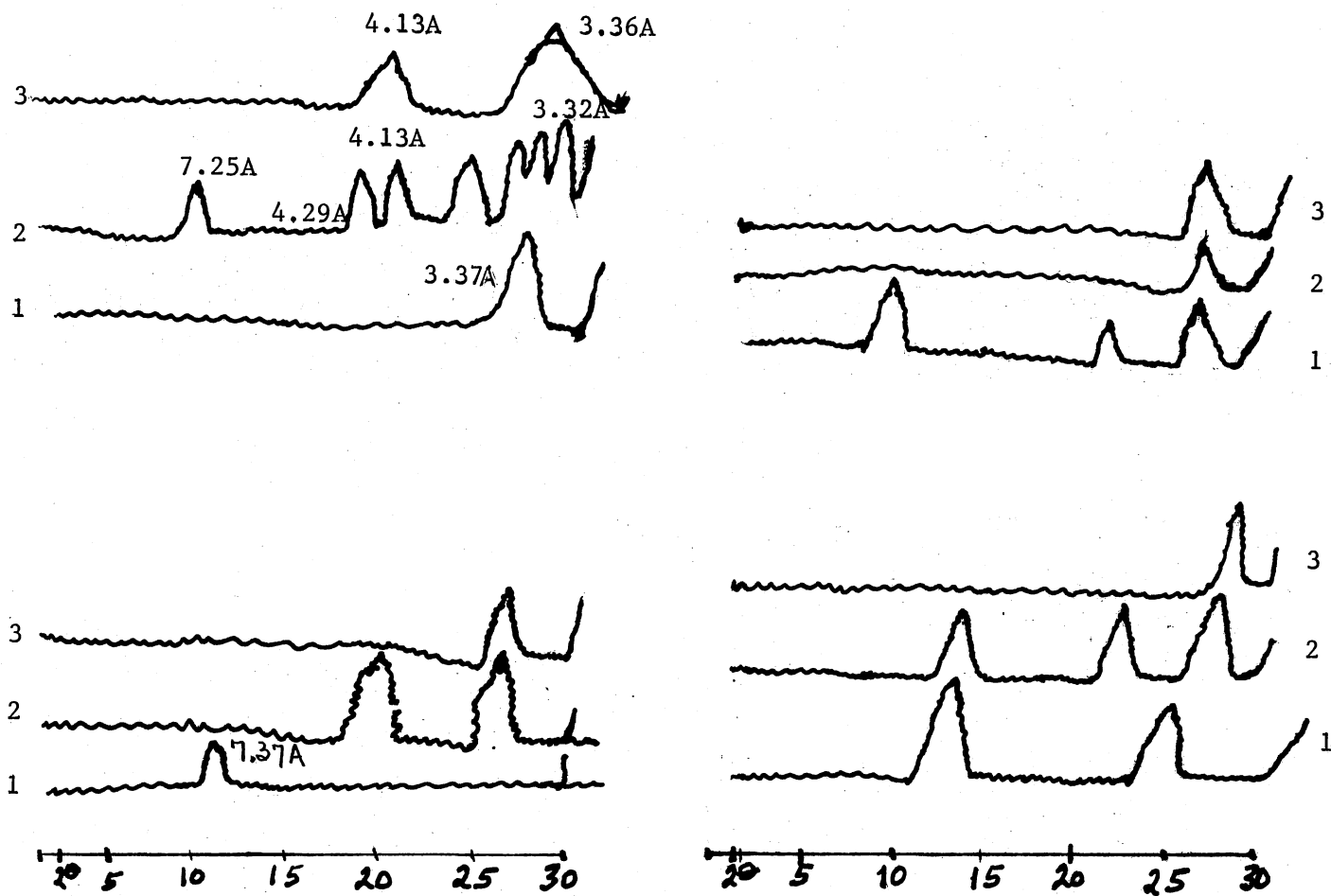


Figure 1. X-ray Diffractograms for the Comasadu I Soil: (1) Ca-Saturated, (2) K-Saturated (Air-Dried), (3) K-Saturated and Heated to 500°C. Measurements in Angstroms.

the kaolinite peaks but quartz peak was again found at 3.36A.

Figure 2 shows x-ray diffractograms for the Foya Model. The calcium saturated sample of the fine clay fraction of the 33-60 cm depth revealed a low intensity peak at 7.37A for kaolinite and the second order maximum for kaolinite at 3.62A. Potassium saturation gave results similar to those of calcium saturated samples. All of the kaolinite peaks were destroyed when the potassium sample was heated to 500°C. The coarse clay fraction when calcium treated produced a kaolinite peak or metahalloysite at 7.31A and a 3.60A for the second order maximum of Kaolinite. Quartz was identified as a 3.40A. The third order peak of the 14A minerals (montmorillonite, vermiculite, and chlorite), which probably is vermiculite, was identified at a low intensity of 4.92A. Potassium saturation of this sample showed kaolinite at both 7.37A and the second order maximum at 3.62A. The kaolinite peaks collapsed when the sample was heat treated, and the quartz peak was found at 3.36A. When the fine clay fraction of the subsurface (60-120 cm) for the Foya Model was calcium saturated, kaolinite or metahalloysite was found at 7.37A and a second order maximum at 3.60A. A low intensity peak for the 14A minerals probably vermiculite or chlorite was produced as the third order peak at 4.92A. Potassium saturation also produced a kaolinite peak at 7.37A and the second order maximum of kaolinite at 3.62A. No peak appeared when the k-saturated sample was heated to 500°C. Calcium saturation of the coarse clay fraction resulted in a 7.37A peak for kaolinite and the second-order maximum for kaolinite at 3.63A. The presence of the 14A minerals probably chlorite was found as a low intensity third order peak of 4.92A. Potassium saturation of the

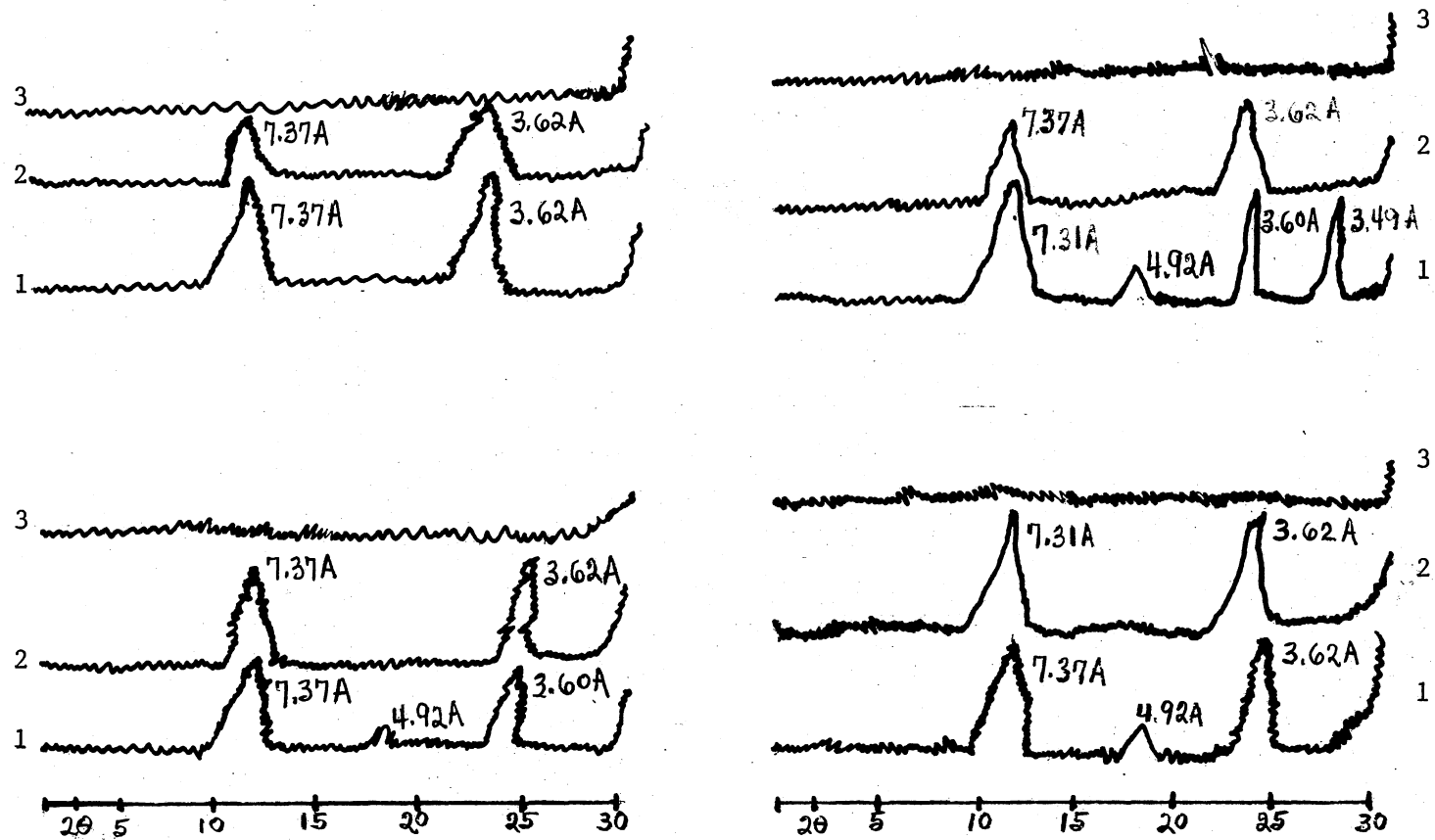


Figure 2. X-ray Diffractograms for the Foya Model III Soil Measured in Angstroms.  
 (1) Ca-Saturated, (2) K-Saturated (Air-Dried), and (3) K-Saturated and Heated to 500°C.

sample revealed a kaolinite peak at 7.31A and second-order maximum of kaolinite at 3.62A. Heat treatment collapsed all peaks found in the sample.

X-ray diffraction patterns for the Foya Deep soil are shown in Figures 3 and 4. Calcium saturation of the fine clay fraction of the surface (0-19 cm. depth) revealed a peak for kaolinite at 7.25A and the second-order maximum at 3.59A. Potassium saturation and heating of the potassium saturated sample resulted in loss of the kaolin minerals. Calcium saturation of the coarse clay fraction gave a high intensity peak for kaolinite at 7.31A and the second-order maximum of kaolinite at 3.62A. A third-order peak for the 14A minerals probably vermiculite or chlorite was found at 4.92A. Potassium-saturation of this sample was similar to the calcium treatment. All peaks collapsed upon heating of the potassium saturated samples which verifies that they were kaolinite peaks. Calcium saturation of the fine clay fraction from the 18-38 cm depth showed a kaolinite peak at 7.25A, the second-order maximum of kaolinite at 3.59A and quartz at 4.21A and 3.35A. Kaolinite was found at 7.25A and quartz at 3.35A when this sample was K-saturated and heat treatment collapsed all existing peaks. Calcium saturation of the coarse clay fraction produced a high intensity peak for kaolinite at 7.31A and the second-order maximum of kaolinite at 3.62A. A low intensity peak for the third-order of 14A minerals was found at 4.92A. K-saturation of the coarse clay fraction yielded a kaolinite peak at 7.31A and the second-order maximum at 3.60A and a third order peak for the 14A minerals was found at 4.92A. Heating of the sample to 500°C caused disappearance of all peaks in the sample.

X-ray diffraction patterns for the subsurface (38-72 cm and 105-

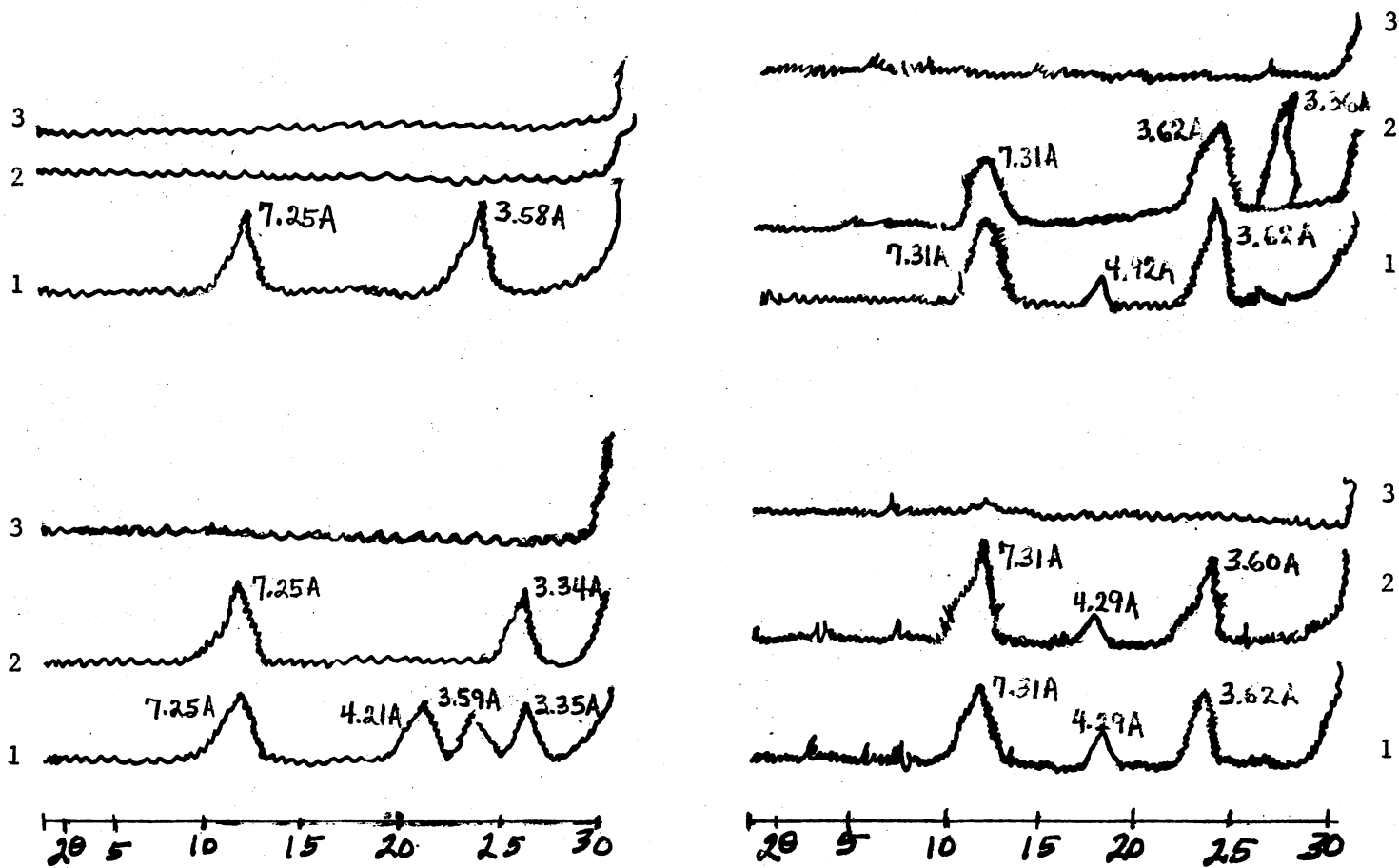


Figure 3. X-ray Diffractograms for the Foya Deep IV Soils Measured in Angstroms. (1) Ca-Saturated, (2) K-Saturated (Air-Dried), and (3) K-Saturated and Heated to 500°C.

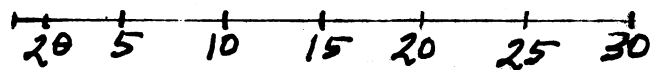
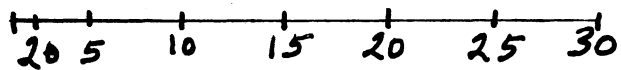
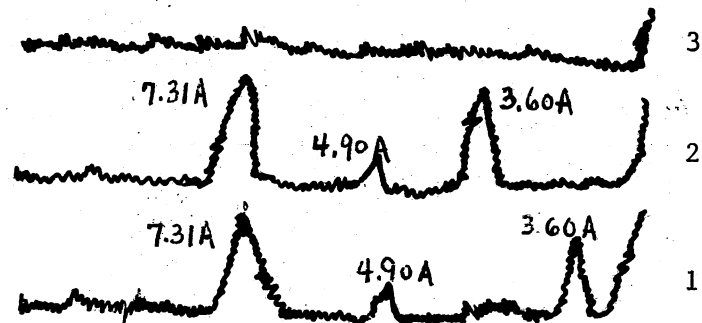
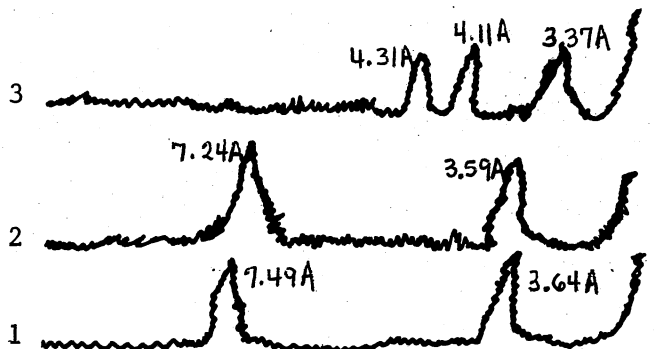
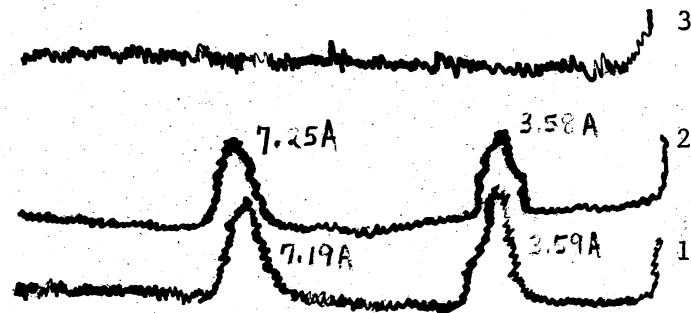
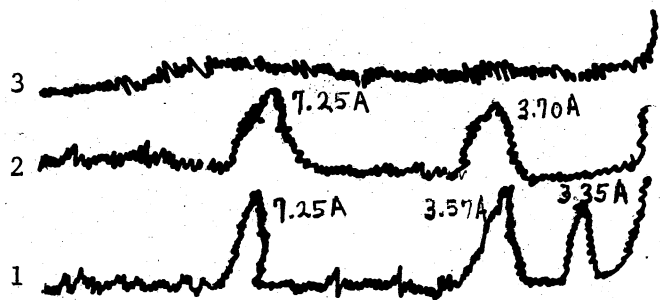


Figure 4. X-ray Diffractograms for the Foya Deep IV Soil Measured in Angstroms. (1) Ca-Saturated, (2) K-Saturated, and (3) K-Saturated and Heated to 500°C.



40 cm depth) of the Foya Deep are given in Figure 4. Calcium saturation of the fine clay fraction of the top portion of this profile (38-72 cm) gives a high intensity kaolinite peak at 7.25A while the second-order maximum of kaolinite appeared at 3.75A. Quartz was identified as a 3.35A peak. Potassium saturation of the sample did not change the position of the first-order peak of kaolinite but the second order of kaolinite was found at 3.70A. Heating the potassium saturated sample completely destroyed the peaks. When the coarse clay portion was calcium saturated, a kaolinite peak of 7.19A with high intensity was produced. The second-order maximum of kaolinite was found at 3.59A and heat treatment of the potassium saturated sample destroyed all kaolinite peaks. Calcium saturation of the fine clay fraction of the next layer (105-140 cm depth) revealed a kaolinite peak at 7.49A and the second-order maximum of kaolinite at 3.64A. When the sample was potassium saturated, the kaolinite peaks moved to 7.25A for the first order and 3.59A for the second-order maximum. Only the quartz peak was identified at 3.37A, 4.11A, and 4.31A when the sample was heated to 500°C. Calcium-saturation of the coarse clay fraction shows a kaolinite peak at 7.31A and the second-order maximum of kaolinite at 3.60A and a 4.90A peak for the third order of the 14A minerals probably chlorite appeared. Potassium saturation of this fraction did not change the results obtained when it was calcium treated but these peaks were destroyed when heated to 500°C.

X-ray diffraction analysis for the Makana soil is shown in Figure 5. The deeper portion of the Makana soil and surface of the Dalin soil is shown in Figure 6. Calcium saturation for the fine clay fraction of the Makona (0-30 cm depth) shows a broad

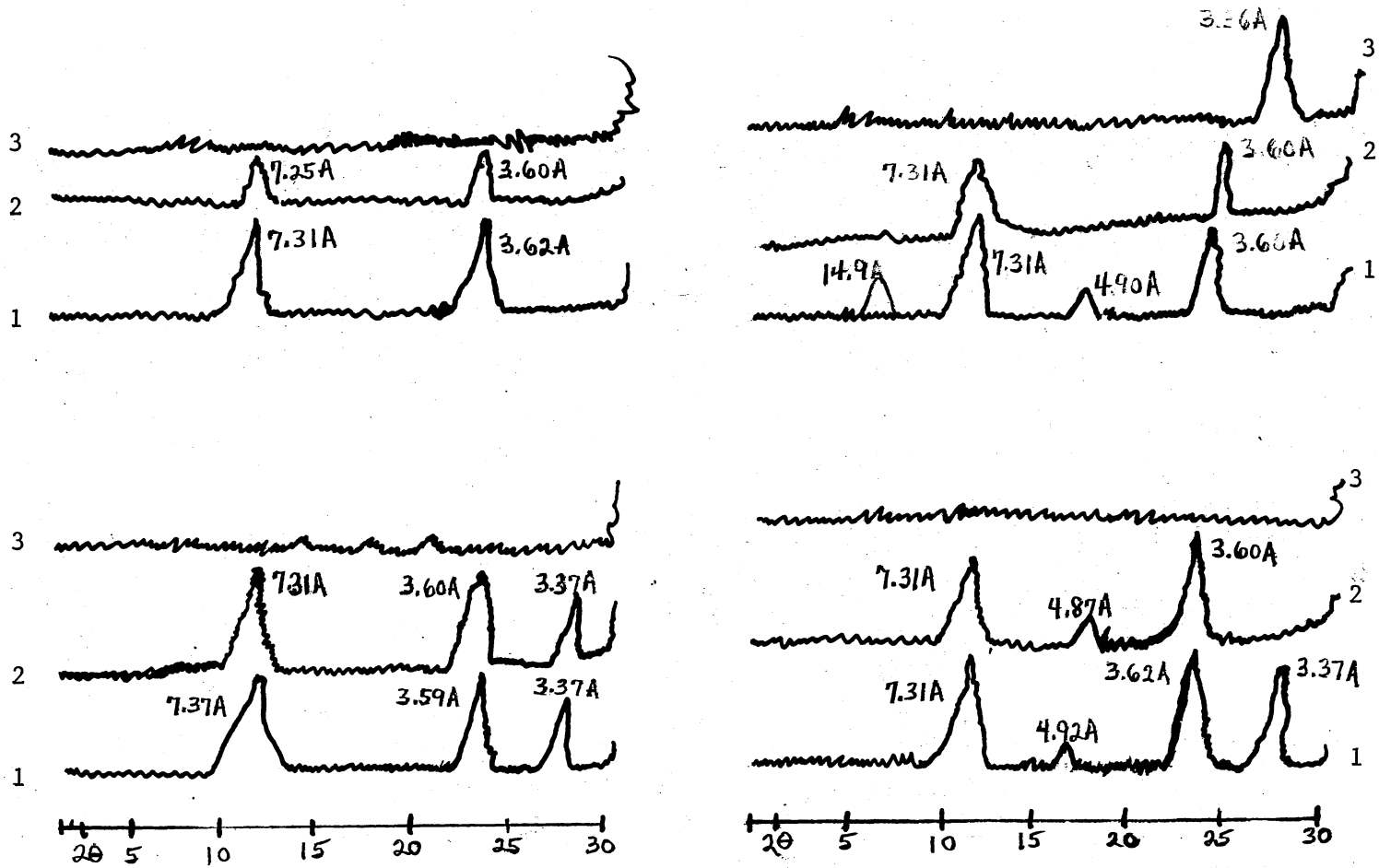


Figure 5. X-ray Diffractogram for the Makona V Soil Measured in Angstroms. (1) Ca-Saturated, (2) K-Saturated (Air-Dried), and (3) K-Saturated and Heated to 500°C.

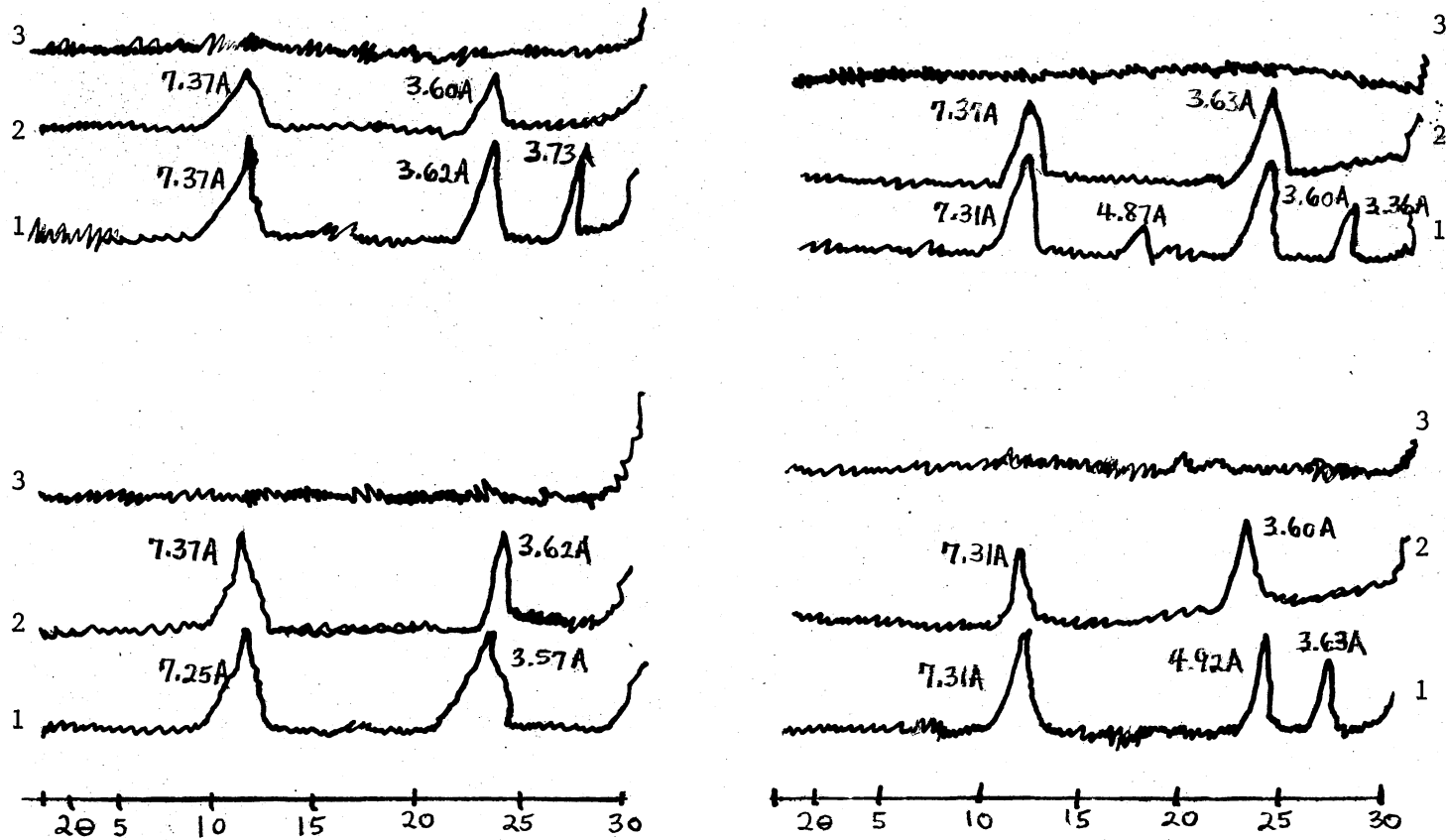


Figure 6. X-ray Diffractograms for the Makona V Deep Subsurface and the Dalin II Surface Soil Measured in Angstroms. (1) Ca-Saturated, (2) K-Saturated (Air-Dried), and (3) K-Saturated and Heated to 500°C.

kaolinite peak at 7.31A (Figure 5) and 3.62A for the second-order maximum of Kaolinite. Potassium saturation produced a kaolinite peak at 7.25A and a second-order maximum of 3.60A. Heating the potassium saturated sample to 500°C collapsed all of the peaks found. Calcium treatment of the coarse clay fraction resulted in a high intensity kaolinite peak at 7.31A and the second-order maximum of kaolinite appeared at 3.60A. A low intensity peak probably the third order of the 14A minerals was found at 4.90A. After the sample was saturated with potassium a kaolinite peak appeared at 7.31A and the second-order maximum at 3.60A. Heat treatment removed all peaks except for quartz which appeared at 3.36A. Calcium saturation of the fine clay fraction for the sample collected from the next layer (30-47 cm. depth) produced a peak of 7.37A for kaolinite. The second-order maximum for kaolinite was found at 3.57A. A low intensity peak for quartz was found at 3.37A. When this sample was potassium saturated, a kaolinite peak appeared at 7.31A and the second-order maximum at 3.59A. Heating the sample to 500°C removed all peaks indicating the presence of kaolinite. The coarse clay fraction when calcium saturated produced a kaolinite peak at 7.37A. A peak for the third-order of the 14A minerals was found at 4.92A. The second order of kaolinite was found at 3.62A peak and a quartz peak was found at 3.37A. After potassium saturation of the samples the kaolinite peak appeared at 7.31A and a second-order maximum at 3.60A. The peak for the third-order of the 14A minerals was found at 4.87. Heat treatment of the sample collapsed all peaks which verifies the presence of kaolinite.

X-ray diffraction analysis of the deep stratum (87-140 cm depth) of the Makona soil is also given in Figure 6. Calcium saturation of

the fine clay fraction produced a low intensity peak for kaolinite at 7.25A and the second-order maximum kaolinite peak at 3.57A. When the sample was potassium-saturated, a high intensity kaolinite peak was found at 7.37A and the second-order maximum kaolinite was found at 3.62A. Heating this sample to 500°C destroyed the kaolinite peaks completely. Calcium saturation of the coarse clay fraction revealed a kaolinite peak at 7.31A and the second-order of kaolinite at 3.62A. The third order of the 14A minerals perhaps chlorite was found at 4.92A. Potassium saturation of the sample produced a high intensity peak for kaolinite at 7.31A and a second-order maximum at 3.60A. A peak for the third order of the 14A minerals was found at 4.90A. Heating the sample to 500°C entirely destroyed these peaks.

Figure 6 also contains an x-ray diffraction pattern for the Dalin soil (0-26 cm deep). The calcium saturated fine clay fraction showed a high intensity peak for kaolinite at 7.37A and a second-order maximum at 3.62A and 3.73A on potassium saturation of the sample. A kaolinite peak at 7.37A and its second-order maximum was observed at 3.60A. Heating to 500°C completely destroyed these peaks which shows that they were kaolinitic peaks. When the coarse clay fraction was calcium saturated it produced a high intensity kaolinite peak at 7.31A and the second-order maximum peak for kaolinite at 3.60A. A low intensity peak for the third order of the 14A minerals was shown at 4.87A. A low intensity quartz peak was found at 3.36A. The potassium saturated sample had a kaolinite peak at 7.37A and a second-order maximum of kaolinite at 3.63A. Heating to 500°C destroyed the kaolin diffraction peaks.

X-ray diffraction patterns for the Kanjo soil is reported in

Figure 7. Calcium saturation of the fine clay fraction of the surface 37 cm depth showed a broad kaolinite peak at 7.25A and a second order maximum of kaolinite at 3.59A. After it was saturated with potassium, a low and broad kaolinite peak appeared at 7.31A and the second-order maximum of kaolinite at 3.59A. Heating the potassium saturated sample to 500°C destroyed all of the kaolinite peaks. The calcium saturated coarse clay fraction of the sample showed a kaolinite peak at 7.37A and a second order maximum at 3.62A. The potassium saturated sample showed the same kaolin peaks. Heating of the potassium-saturated sample to 500°C caused these peaks to disappear. The calcium saturated fine clay portion of the subsurface (68-123 cm depth) soil sample showed a low intensity kaolinite peak at 7.31A and a second-order maximum kaolinite peak at 3.59A. A low intensity kaolinite peak at 7.37A and the second-order maximum kaolinite peak at 3.59 was observed for the potassium saturated sample. Quartz peaks appeared at 3.48A and 3.28A. Heating the sample to 500°C destroyed all kaolinite peaks, however, the quartz peak persisted at 3.37A. The calcium saturated coarse clay fraction of this subsurface soil sample had a kaolinite peak at 7.37A and a second-order maximum at 3.63A. A low intensity peak probably due to 14A minerals was found at 4.92A. The coarse clay potassium saturated sample had a broad and low kaolinite peak at 7.31A and a second order maximum at 3.60A. Heating of the potassium-saturated sample caused all peaks to collapse.

X-ray diffractograms for the N'gisi Konja soil are shown in Figure 8. Calcium saturation of the fine clay fraction of the surface (0-37 cm depth) soil shows a kaolinite peak at 7.37A and the second-order maximum for kaolinite at 3.59A. A low intensity quartz peak was

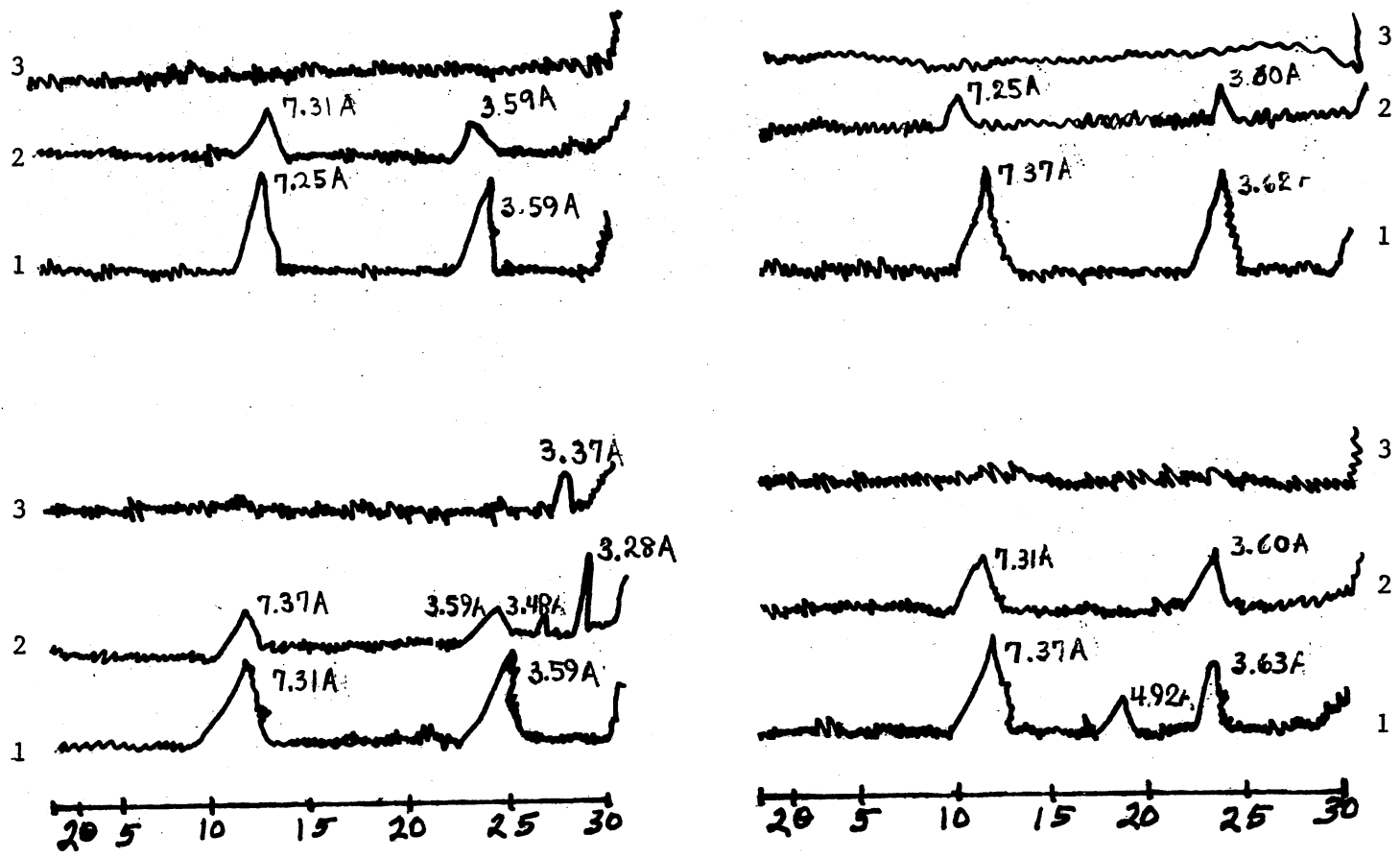


Figure 7. X-ray Diffractograms for the Kanjo VI Soil Measured in Angstroms. (1) Ca-Saturated, (2) K-Saturated (Air-Dried), and (3) K-Saturated and Heated to 500°C.

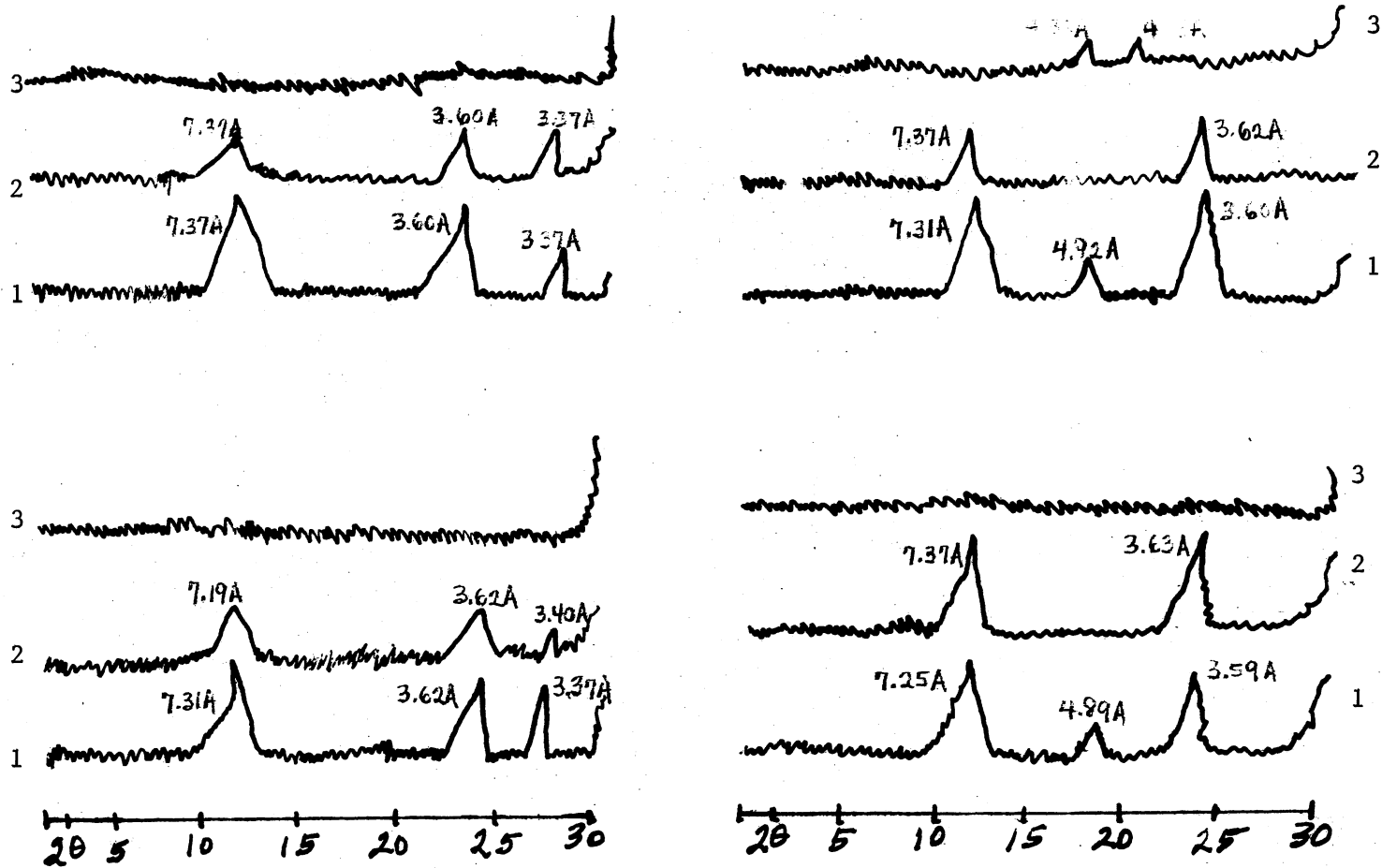


Figure 8. X-ray Diffractograms for the N'gisi Konja VII Soil Measured in Angstroms.  
 (1) Ca-Saturated, (2) K-Saturated (Air-Dried), and (3) K-Saturated and Heated to 500°C.



found at 3.37A. However, potassium saturation of this sample showed a high intensity kaolinite peak at 7.37A and a second order maximum kaolinite peak at 3.60A and the quartz peak was at 3.37A. The calcium saturated coarse clay fraction had a high intensity kaolinite peak at 7.31A and a second-order maximum at 3.60A. A peak for the 14A minerals probably chlorite was observed at 4.92A. The potassium saturated sample gave kaolinite peaks at 7.37A and the second-order maximum at 3.62A. Heating of the potassium saturated sample to 500°C caused the Kaolin peaks to disappear and quartz peaks to remain at 4.13A and 3.33A. The calcium saturated fine clay fraction of the subsurface (37-80 cm depth) sample had a high intensity kaolinite peak at 7.31A and a second-order maximum was identified at 3.62A and the quartz peak was at 3.37A. The potassium saturated sample shows a low intensity kaolinite peak at 7.19A and a second-order maximum at 3.62A but the quartz peak shifted to 3.40A. The kaolin peaks in the potassium-saturated sample disappeared when it was heated to 500°C. The calcium saturated coarse clay fraction had a high intensity kaolinite peak at 7.25A and a second-order kaolinite peak at 3.59A. A peak for the 14A minerals was observed for the third-order at 4.87A. The potassium sample had a kaolinite peak at 7.37A and a second-order maximum at 3.63A and heating the sample destroyed all kaolin peaks.

The x-ray diffraction patterns for the Red Weledu soil is shown in Figure 9. The calcium saturated fine clay fraction of the surface (0-15 cm depth) had a low intensity kaolinite peak at 7.25A and a second-order maximum at 3.59A. The peak for quartz was observed at 3.36A. Kaolinite and quartz peaks did not change when this sample was potassium saturated. The second order maximum of kaolinite was

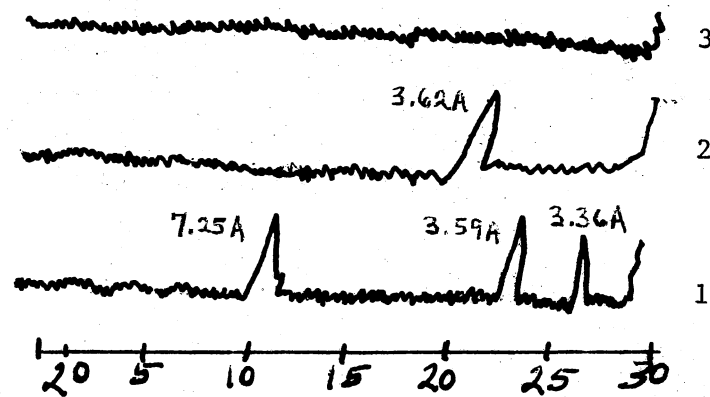
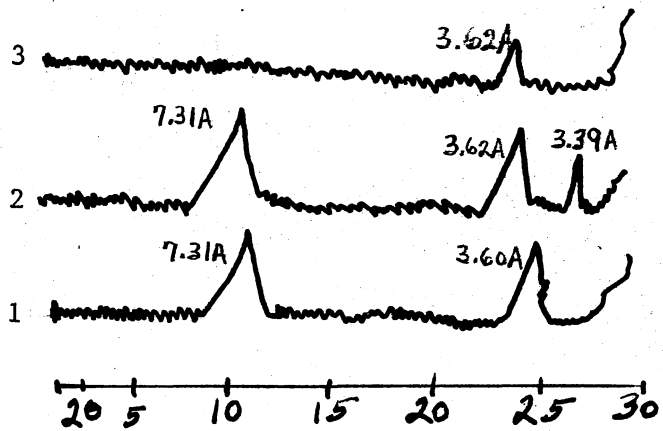
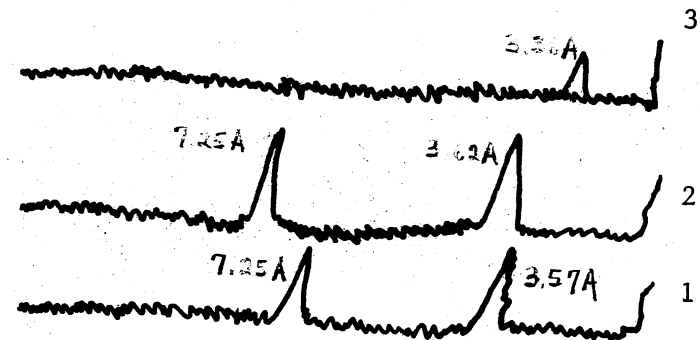
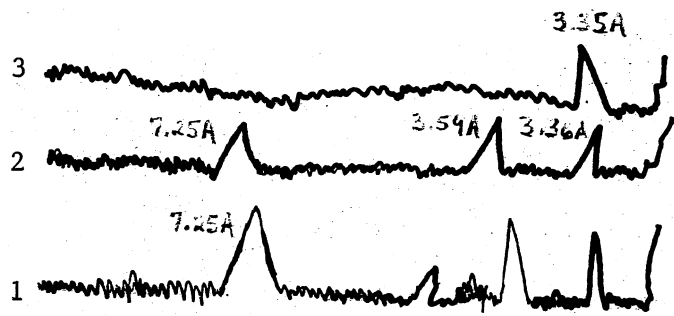


Figure 9. X-ray Diffractograms for the Red Weledu (Foya) VIII Soil Measured in Angstroms.  
 (1) Ca-Saturated, (2) K-Saturated (Air-Dried), and (3) K-Saturated and Heated to 500°C.

produced at 3.59A. The calcium saturated coarse clay fraction had a kaolinite peak at 7.25A and a second-order maximum at 3.57A. The potassium saturated sample had a diffraction maximum at 7.25A for kaolinite (first-order) but the second-order maximum shifted to 3.62A. The heated potassium-saturated sample had a quartz peak at 3.36A while all other peaks were destroyed. The calcium saturated fine clay fraction of the subsurface (62-160 cm depth) showed a kaolinite peak at 7.31A and a second-order maximum at 3.60A. The potassium saturated sample had a kaolinite peak at 7.31A and a second-order maximum at 3.62A and the quartz peak was at 3.39A. Heat treatment of the sample destroyed all peaks but the second order of kaolinite at 3.62A remained and this was probably a third-order chlorite peak and not kaolinite. The calcium saturated coarse clay fraction of this had a kaolinite peak at 7.25A and a second-order maximum at 3.59A. A quartz peak was found at 3.36A. The potassium saturated sample had a second-order maximum for kaolinite at 3.62A. The intensity for the first order of kaolinite was very low and could not be separated from the background. Heating the potassium saturated sample to 500°C caused all peaks to collapse.

X-ray diffraction patterns for the Red Weledu (with stones) soil is shown in Figure 10. The calcium saturated fine clay fraction of the surface 47 cm depth showed a kaolinite peak at 7.37A and a second-order maximum at 3.62A. The potassium saturated sample did not show a change in the results obtained from the calcium saturated sample, however heating the K-saturated sample to 500°C destroyed all peaks except quartz. The calcium saturated coarse clay fraction of this surface soil had a kaolinite peak at 7.49A and a second-order

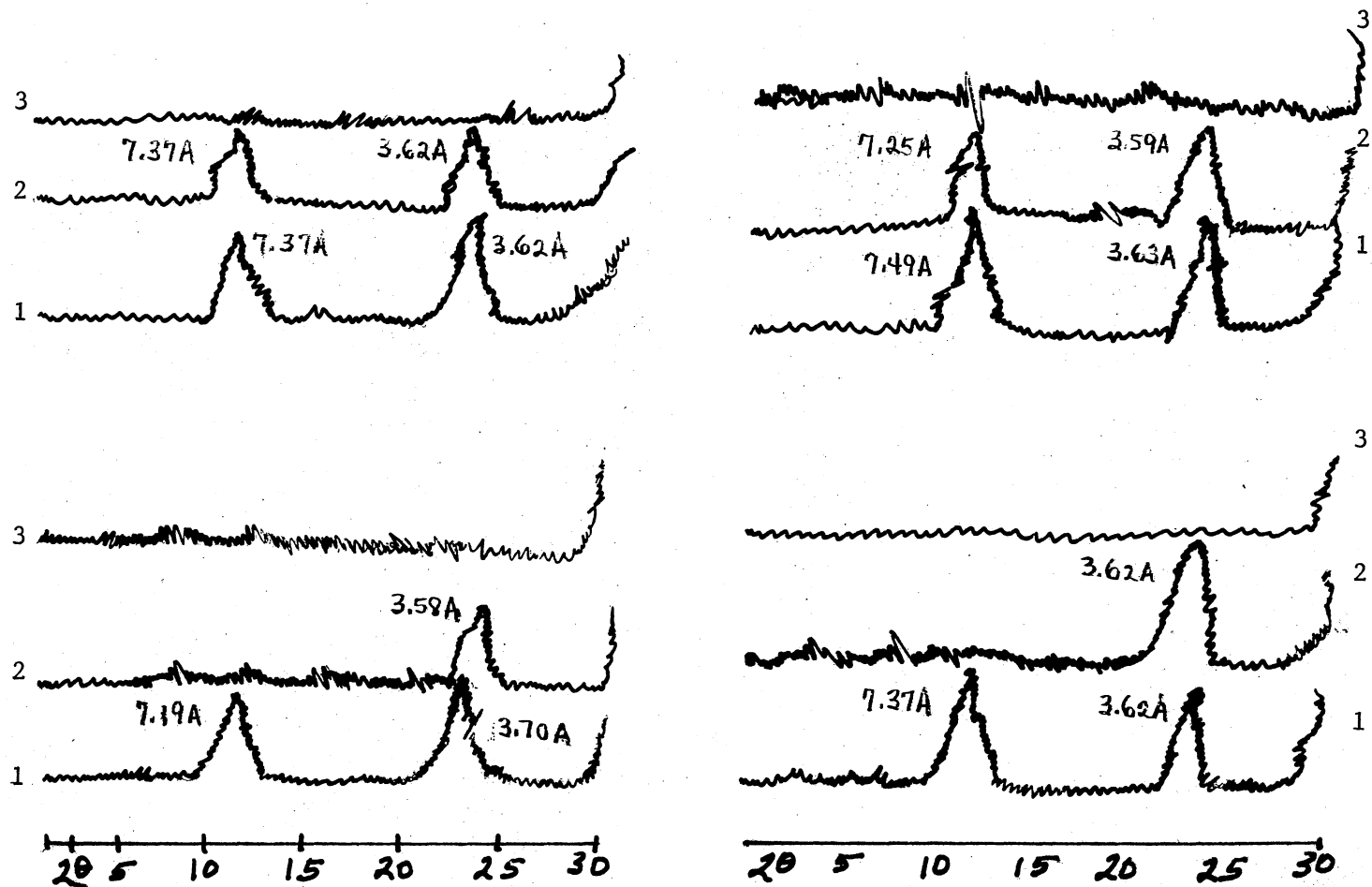


Figure 10. X-ray Diffractograms for the Red Weledu (Stones) IX Soil Measured in Angstroms.  
 (1) Ca-Saturated, (2) K-Saturated (Air-Dried), (3) K-Saturated and Heated to 500°C.

maximum at 3.63A. The potassium saturated sample had a kaolinite peak at 7.25A and a second order maximum at 3.59A. All peaks collapsed when the potassium saturated sample was heated to 500°C. The calcium saturated fine clay portion of the subsurface (47-124 cm depth) had kaolinite peaks at 7.19A and 3.70A for the second-order maximum. The potassium saturated sample gave only the second-order maximum. The potassium saturated sample gave only the second-order maximum kaolinite peak at 3.59A and heating of the potassium saturated sample to 500°C caused all kaolin peaks to disappear. The clay fraction of this sample was treated in the same manner as the fine clay fraction. The first and second-order peaks of kaolinite were found at 7.37A and 3.62A, respectively. The potassium-saturated sample had a second-order maximum for kaolinite at 3.62A. Heating the potassium-saturated sample to 500°C collapsed all kaolin peaks.

X-ray diffractograms for the Yellow Weledu soil are shown in Figure 11. The calcium saturated fine clay fraction of the surface 36 cm depth had a first-order of kaolinite peak at 7.25A and a second-order maximum at 3.59A. A low intensity third-order peak for the 14A clay minerals which was probably chlorite was observed at 4.92A. The potassium saturated sample had a kaolinite peak at 7.31A and a second-order maximum at 3.62A. A low intensity quartz peak appeared at 3.36A. Heating the potassium saturated coarse clay fraction of this sample had first-order kaolinite peaks at 7.25A and a second order maximum kaolin peak at 3.56A. The quartz peak was found at 3.37A. The potassium saturated sample had a high intensity kaolinite peak at 7.25A and a second-order maximum at 3.60A. A low intensity third-order 14A clay mineral peak probably for vermiculite or chlorite

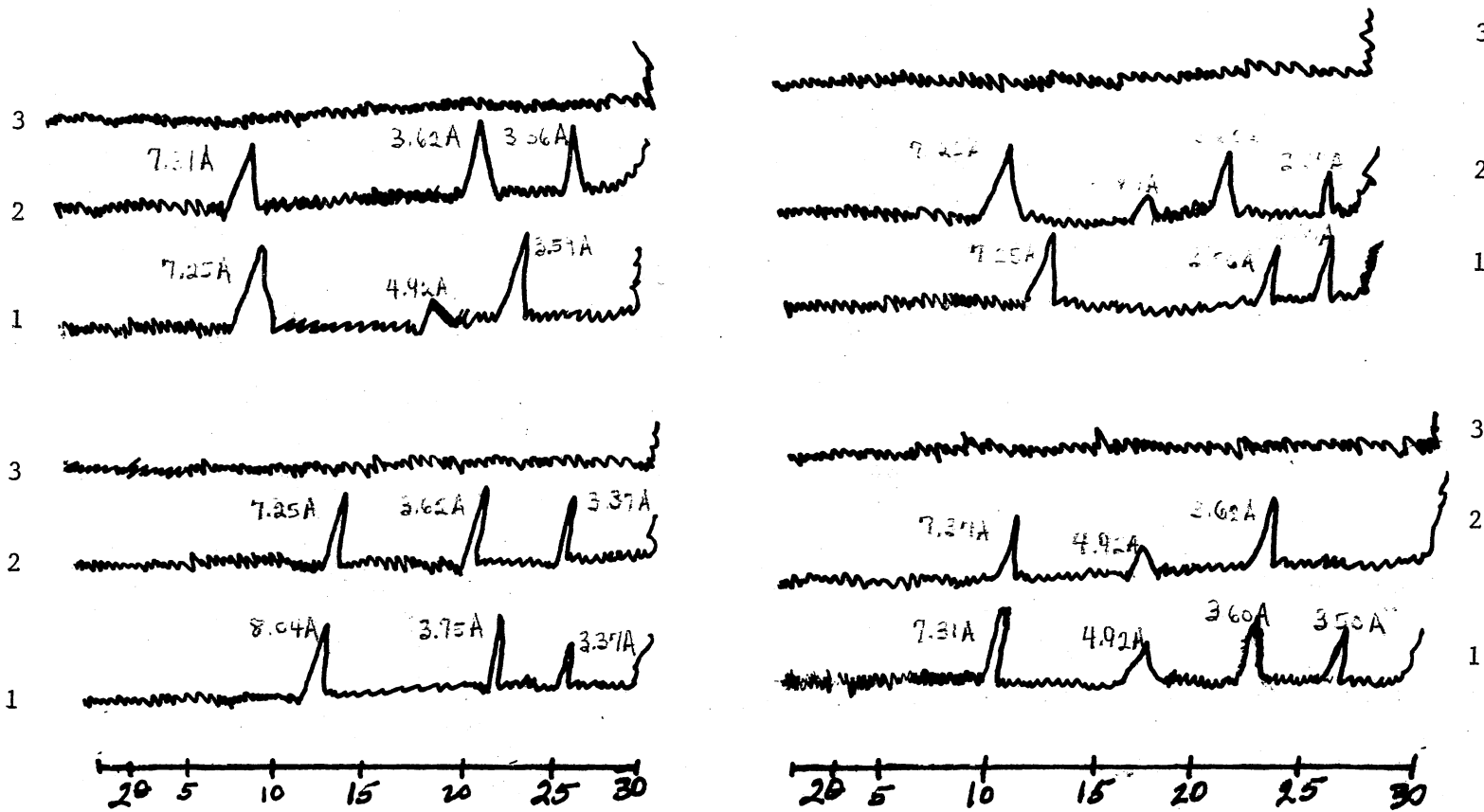


Figure 11. X-ray Diffractograms for the Yellow Weledu X Soil Measured in Angstroms  
 (1) Ca-Saturated, (2) K-Saturated (Air-Dried), and (3) K-Saturated and Heated to 500°C.

was found at 4.87A and the quartz peak was at 3.37A. Heating the potassium saturated sample completely destroyed all peaks found. The calcium saturated fine clay fraction of the subsurface (36-125 cm depth) had a low intensity peak at 8.04A which was probably kaolinite. The second-order maximum kaolinite peaks were found at 3.75A and the saturated sample had a kaolinite peak at 7.25A and a second-order maximum at 3.62A and a quartz peak at 3.37A. The potassium saturated and heated sample showed all peaks to be collapsed. The calcium saturated coarse clay fraction had a high intensity kaolinite peak at 7.31A and a second-order maximum at 3.60A. The third-order of the 14A clay mineral peak was found at 4.92A. The potassium saturated sample had a kaolinite peak at 7.37A and a second-order maximum at 3.62A. A low intensity peak for the third-order of the 14A minerals was observed at 4.92A. The heated potassium saturated sample showed all kaolinite peaks to be collapsed.

## CHAPTER V

### SUMMARY AND CONCLUSION

The soils studied in this investigation were all high in clay and sand. They might be texturally called sandy clays, clays, or clayey soils. These soils are very acid in reaction. The average pH (1:1 in water) ranges from 5.93 to 4.50 and from 5.04 to 4.00 (1:1 in 1 N KCl). Exchangeable acidity ( $Al^{+} + H_3O^{+}$ ) content for all soils was found to be very high which means that a greater portion of the exchange complex of these soils is saturated with exchangeable hydronium and/or aluminum ions. Although, all of these soils are extremely acid, the Foya Model soil was found to be the most acid while Mokana, Konjo, Red Weledu and Red Weledu with stones were only slightly acid.

The cation exchange capacities of these soils were found to be extremely low. On an average basis, the cation exchange capacities of these soils fall within the range of 3.56 m.e./100 grams to 7.15 m.e./100 grams. The Red Weledu soil has the highest average CEC while the Kanjo soil has the lowest. These figures are extremely low if compared with soils in temperate humid areas but are similar to results obtained in other tropical areas. These soils are depleted of bases, however, calcium continues to be the dominant cation of all soils. Of the major essential elements, potassium was the lowest of all soils both on an average and an individual sample basis. The micronutrients are also deficient in these soils. The values obtained for all trace



elements, do not meet the requirement quoted by Tucker and Baker (7) as adequate for optimum plant growth. The percent base saturation of these soils is also very low due to base deficiency. Although the percent base saturation for the Comasadu, Foya Deep, and Red Weledu/stones exceeds 50 percent, it is believed that these higher than expected values are maybe due to experimental errors.

Phosphorus and nitrogen contents are very low in these soils but percent organic matter content is high. Except for the sample collected from the 50-90 cm depth of Comasadu soil which has a total phosphorus content of 131.0 ppm, all other samples contain less than 131.0 ppm total phosphorus. Some samples have total phosphorus values as low as 1 ppm or lower. The Comasadu soil can be said to be higher in phosphorus content than the rest of the soils in this investigation. The Foya Model soil ranks second in phosphorus content. It was found that most of the phosphorus in these soils is in the organic form rather than a form available for plant use. When averages are considered, the Foya Model soil has the highest amount of available phosphorus. All of these soils are extremely low in percent total nitrogen. The percent organic matter content of these soils is very high. It ranges from 0.17 in the 124 cm depth in the Red Weledu/Stones to 4.18 in the first 10 cm depth of the Comasadu soil. The percent organic carbon content is low in all soils. The carbon:nitrogen ratio is high in many of these soils such that mineralization of native nitrogen hardly occurs. The Comasadu soil has the highest carbon:nitrogen ratio of 1: 68.0 in its surface 10 cm depth and the Red Weledu soil with 1: 62.0 in its surface 15 cm depth is second and Dalin with 55.0 in the first 26 cm depth is third. Although these values

decreased with depth, mineralization in the surface layer of these soils is not likely to occur.

With regard to nutrient element requirements all of the soils in the study were efficient in removing the nutrients added to the extracting solution as outlined by Baker (5,6). This demonstrates that these soils are deficient in these nutrient elements according to Baker (5,6). Calcium however, was the least removed by all soils perhaps because it is the dominant cations in these soils. It can be suggested that fertilizer materials for these soils in excess of the amount (Table I) of nutrient elements included in the solution for testing these soils for the Baker's test would prove to be profitable.

Total phosphorus correlated significantly with available phosphorus, organic phosphorus, organic matter and Baker's calcium. Unless the soil factors are disregarded, total phosphorus did not correlate significantly with the other remaining tests, for example, exchangeable calcium, magnesium, and percent total nitrogen. Correlations were found between available phosphorus and organic phosphorus and organic matter. Organic phosphorus correlated significantly with organic matter and Baker's magnesium and organic matter also correlated significantly with Baker's manganese and exchangeable sodium. Other correlations of interest are reported in Table XXVI. It was observed that when soil effects are removed, many of the tests will correlate significantly with other tests. For example, when soil effects were removed, total phosphorus was found to correlate significantly with percent total nitrogen, exchangeable calcium, and with other tests, it did not, when soil factors were involved. Available phosphorus was also found to be

correlated significantly with percent total nitrogen, Baker's calcium, magnesium, exchangeable calcium, magnesium, and other tests. These correlations are reported in Tables XXVII through XXXVII.

Metahalloysite or kaolinite was found to be the dominant clay minerals in all of the samples examined for clay mineral characteristics. Low intensity x-ray diffraction peaks for the third-order of the 14A clay minerals were found in many of the soils studied. This probably indicates that clay minerals such as montmorillonite, vermiculite, and chlorites might be present in these soils but in very small amounts. Most such minerals have been eluviated out of these soils, however, traces can be detected by x-ray. Quartz, was also found to be dominant in the clay fractions of these soils.

It has been shown that the soils in this study are highly weathered and are very deficient in elements required by plants. It was also shown that most of the weatherable minerals have been removed from these soils by weathering. The high clay and low silt contents of these soils is additional proof that these soils can be said to be highly weathered and probably very old. The low nutrient element content is largely due to excessive leaching by long periods of torrential tropical rainfall each year and the lack of weatherable minerals rich in these elements.

It is suggested that a sound fertilizer program be instituted if these soils are to be cultivated on a commercial or highly productive basis. Liming programs must be an indispensable aspect of the fertilizer scheme. Banding of fertilizers instead of broadcasting will be much preferred after consideration of costs. Cultivation of deep rooted crops where fertilizer is not feasible is recommended

for these soils rather than shallow rooted crops. Cultural methods aimed at preventing erosion will be of great help.

In brief, it can be said that the soils of Liberia are poor for intensive crop production but they can be made productive if a fertilizer scheme is adopted where economy of application and management is of a high order. In other areas, these soils can be said to have some engineering advantages for construction, that is, these soils can be very stable for engineering purposes.

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APPENDIX

## Profile Description

<u>Sample No.</u>	<u>Soil</u>	<u>Depth cm</u>	<u>Description</u>
1.	Comasudu	0-10	Reddish brown (2.5YR 4/6) Sandy clay loam, dark reddish brown (5YR 3/4) moist; slightly sticky and plastic when wet; pH 5.10.
2.		10-20	Yellowish red (5YR 5/8) sandy clay loam, yellowish red (5YR 4/6) moist; sticky and plastic; pH 5.10.
3.		20-50	Reddish yellow (5YR 7/8) sandy clay; yellowish red (5YR 5/8) moist; pH 5.40.
4.		50-90	Reddish yellow (5YR 7/8) sandy clay; yellowish red (5YR 5/8) moist; sticky and plastic; pH 5.50.
5.		90-140	Light red (1.0YR 6/8) sandy clay, red (10YR 4/6) moist; sticky and plastic; pH 5.80.
6.	Dalin II	0-26	Gray (7.5YR 6/1) sandy clay loam, dark gray (7.5YR 4/1) moist; pH 4.50.
7.	Foya Model III	33-60	Pale brown (10YR 6/3) sandy clay; dark grayish brown (10YR 4/2) moist; very sticky and plastic; pH 5.20.
8.		60-104	Very pale brown (10YR 7/4) sandy clay; yellowish brown (10YR 5/4) moist; very sticky and plastic; pH 5.40.
9.		104-120	Very pale brown (10YR 7/4) sandy clay, yellowish brown (10YR 5/4) moist; very sticky and plastic; pH 5.7.

<u>Sample No.</u>	<u>Soil</u>	<u>Depth cm</u>	<u>Description</u>
10.	Foya Deep IV	0-18	Brown (10YR 5/3) sandy clay, dark brown (10YR 3/3) moist; slightly sticky and plastic; pH 4.6.
11.		18-38	Brown (10YR 5/3) sandy clay, brown (10YR 4/3) moist; slightly sticky and plastic; pH 4.9.
12.		38-72	Yellow (10YR 7/6) sandy clay, yellowish brown (10YR 5/4) moist; sticky and plastic; pH 5.1.
13.		72-105	Yellow (10YR 7/6) sandy clay, brownish yellow (10YR 6/6) moist; sticky and plastic; pH 5.6.
14.		105-140	Reddish yellow (7.5YR 6/8) sandy clay, strong brown (7.5YR 5/8) moist; sticky and plastic; pH 5.8.
15.		18-38	Grayish brown (10YR 5/2) sandy clay loam, very dark grayish brown (10YR 3/2) moist; slightly sticky and plastic; pH 5.7.
16.	Mokana V	0-12	Grayish brown (10YR 5/2) sandy clay loam, very dark grayish brown (10YR 3/2) moist; sticky and plastic when wet; pH 4.8.
17.		12-30	Light yellowish brown (10YR 6/4) clay, yellowish brown (10YR 5/4) moist; sticky and plastic when wet; pH 5.4.
18.		30-47	Yellow (10YR 7/6) clay loam brownish yellow (10YR 6/5) moist; sticky and plastic when wet; pH 6.0.

<u>Sample No.</u>	<u>Soil</u>	<u>Depth cm</u>	<u>Description</u>
19.	Mokana V	47-87	Yellow (10YR 7/6) clay loam, brown yellow (10YR 6/6) moist sticky and plastic when wet; pH 6.1.
20.		87-140	Yellow (10YR 8/6) clay, yellow (10YR 7/6) moist; sticky and plastic when wet; pH 5.8.
21.	Konjo VI	0-8	Light Yellowish brown (10YR 6/4) sandy clay, yellowish brown (10YR 5/4) moist; sticky and plastic when wet; pH 5.1.
22.		8-37	Light yellowish brown (10YR 6/4) sandy clay, yellowish brown (10YR 5/4) moist; sticky and plastic when wet; pH 5.3.
23.		37-68	Reddish yellow (7.5YR 6/8) clay, strong brown (10YR 5/4) moist; sticky and plastic when wet; pH 6.2.
24.		68-101	Reddish yellow (5YR 6/8) clays yellowish red (5YR 5/6) moist; sticky and plastic when wet; pH 6.2.
25.		101-123	Reddish yellow (5YR 6/6) clay, yellowish red (5YR 4/6) moist; sticky and plastic when wet; pH 6.6.
26.	N'gisi Konja VII	0-10	Light brownish gray (10YR 6/2) sandy clay, very dark grayish brown (10YR 3/2) moist, slightly sticky and plastic when wet. pH 4.8.
27.		10-37	Gray (10YR 6/1) dry sandy clay, and gray (10YR 5/1) moist, sticky and plastic when wet, pH 4.8.



<u>Sample No.</u>	<u>Soil</u>	<u>Depth cm</u>	<u>Description</u>
28.	N'gisi Konja VII	37-80	Whitish gray (10YR 8/1) clay, light gray (10YR 6/1) moist; sticky and plastic when wet; pH 4.8
29.	Red Weledu (Foya) VIII	0-15	Strong brown (7.5YR 5/6) sandy clay, dark brown (7.5YR 4/4) moist; slightly sticky and plastic when wet; pH 5.0.
30.		15-62	Reddish yellow (5YR 6/8) sandy clay, yellowish red (5YR 5/8) moist; sticky and plastic when wet. pH 5.5.
31.		62-135	Reddish yellow (5YR 6/8) sandy clay, yellowish red (5YR 5/6) moist; sticky and plastic when wet; pH 6.2.
32.		135-160	Reddish yellow (5YR 7/8) clay, yellowish red (5YR 5/6) moist; sticky and plastic when wet. pH 5.7.
33.	Red Weledu/ Stones IX	0-25	Light yellow brown (10YR 6/4) sandy clay, brown (10YR 4/3) moist; sticky and plastic when wet pH 6.1.
34.		25-47	Brown (10YR 5/3) sandy clay, dark brown (10YR 4/3) moist; stocky and plastic when wet; pH 5.5.
35.		47-102	Reddish yellow (7.5YR 6/8) clay, strong brown (7.5YR 5/6) moist sticky and plastic when wet; pH 5.9.
36.		102-124	Reddish yellow (7.5YR 7/8) clay, strong brown (7.5YR 5/8) moist; pH 6.2.

<u>Sample No.</u>	<u>Soil</u>	<u>Depth cm</u>	<u>Description</u>
37.	Yellow Weledu X	0-22	Brown (10YR 5/3) sandy clay loam, very dark grayish brown (10YR 3/2) moist; sticky and slightly plastic when wet; pH 4.6.
38.		22-36	Light yellowish brown (10YR 6/4) sandy clay, dark yellowish brown (10YR 4/4) moist; sticky and plastic when wet; pH 4.9.
39.		36-74	Yellow (10YR 7/6) clay, yellowish brown (10YR 5/4) moist; sticky and plastic when wet; pH 5.0.
40.		74-125	Yellow (10YR 7/6) clay, brownish yellow (10YR 6/6) moist; pH 6.0.

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