

THE CHEMISTRY OF POTASSIUM AND NON-CRYSTALLINE
COLLOIDS IN ETHIOPIAN SOILS

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COLLOIDS IN ETHIOPIAN SOILS

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"The greater need today is among the people, with those who work the soil, who provide the nourishment and sustenance upon which Ethiopia feeds."

Haile Selassie I, Emperor of Ethiopia
In Throne Speech for 1965.

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PART I. INTRODUCTION

The economy of Ethiopia is heavily dependent on agriculture; and this basic industry is seemingly to command the lead in importance for a good many years to come. This being the case, the emphasis of modern technical "know-how" in improving Ethiopian agriculture obviously needs to be of the highest order.

It goes without saying that as in many other countries, the soils in Ethiopia represent the essence of the agricultural development.

Generally speaking, Ethiopia is endowed with good agricultural soils; however, increasing their productivity level is a must in order to realize more yield per unit "gasha." To achieve this goal it is necessary to establish the basic information that would be invaluable in making future recommendations. The study of the chemistry of potassium and the non-crystalline colloids of these soils is one such undertaking.

The characterization of soil properties by chemical and physical procedures has been most useful for understanding the nutrition of plants growing in soil. The determination of clay mineral type and quantity has allowed us to predict the soluble element supplying power of a soil. For example, the lime requirement of soils vs. plant requirement changes radically with clay mineral types. Soils high in kaolinite provide adequate calcium for plant growth if the clay saturation is as low as 50% while soils high in montmorillonite do not provide adequate calcium for plant growth unless the percent calcium saturation is over 70%.

However, most soils do not contain the sharply defined clay

minerals of the geologist and mineralogist.

The soil chemist must identify these minerals as soil-kaolinite or soil-montmorillonite, etc. In many soils psuedo-clay minerals exist that are so poorly crystallized that they have been given the name allophane, which have been identified by Aomine (2)* and Jackson (27) as non-crystalline clay minerals. Many soils derived from volcanic debris of recent origin are high in allophane and can be identified and measured indirectly by chemical means. Birrell and Gradwell (6) found that soils high in allophane gave high but variable cation exchange capacities which varied with the saturating cation, normality of leaching solution, and hydrolysis of the exchange complex. Jackson (27) has described a procedure for the determination of the pH dependent charge and delta-value exchange capacity in soils and the determination of allophane.

In general, soils of the tropics are often thought to be latosolic; however, latosols are not confined to the tropics, nor are all tropical soils latosols. Many of the soils of Ethiopia are known to be very high in clay and in some cases relatively low in organic matter (40) and that many of the soils are known to be high in cation exchange capacity (13, 40, 41).

Dark-colored soils from New Zealand (6), Japan (2), and Turkey (26) may be high in clay and exchange capacity, but the fertility of these soils are radically different, and the types of clay minerals range from highly crystalline to amorphous. This may or may not be the case of the dark-colored soils of Ethiopia, which is worth investigating.

* Numbers in parentheses indicate literature cited.

To test the hypothesis that allophane may be found in Ethiopian soils of volcanic parent material a soil test type experiment was necessary. If these soils are derived from volcanic-basaltic parent materials, they should be relatively low in potassium particularly potassium ions buried in the clay mineral lattice. Garman (18) has presented a procedure for identifying the several kinds of replaceable and structural potassium in soils. By use of this procedure it was possible for him to identify indirectly the types of soil minerals present and the rate of release of potassium to plants. By use of this procedure Garman could predict plant uptake of potassium very accurately with a correlation coefficient of 0.96. Soils studied have essentially the same parent material but the stage of development ranges from latosols to chernozemic type soils.

Aluminum interlayering in soil clays has been widely reported particularly for 14 Angstrom clays (26, 46). Jackson (26) reports that montmorillonitic soils from Turkey do not obey the generally accepted concept of extreme plasticity of soils with more than 30% by weight of montmorillonite. Many of the Black Soils of Ethiopia are neutral to basic in reaction, contain more than 60% clay particularly in the Debre-Zeit area according to Murphy (40). These soils are quite granular, not plastic considering the very large amount of clay and average 2% organic matter. It appeared obvious that these soils are montmorillonitic but the quantity of organic matter appeared to be quite low for soils with this quantity of clay. Therefore, it seemed obvious that these high clay, highly granular soils may contain hydroxide interlayers which may contribute more to their stability and granularity than organic matter. The hydrated aluminum oxide bonding between the allophanic clay particle

and soil organic matter (humus) has been proposed as a part of the mechanism responsible for the extreme granularity of the Ando soils of Japan (26) (Ando in the Japanese language is "dark soil"). It was proposed here that hydrated aluminum oxide interlayers on the montmorillonitic "Black Soils" of the Ethiopian Plateau may be responsible for the granularity of these soils. These statements are not meant to imply that soil organic matter is not important in these soils but the relatively small amount of soil organic matter may not adequately explain the granularity of these soils. Turkish soils from basalt have been shown to be highly montmorillonitic, have a sharp 18 Angstrom C-dimension X-ray diffraction peak and have a high degree of aluminum hydroxide interlayering (26).

The specific objective of this thesis is to attempt to explain high granularity, extent of aluminum interlayering in the clay fraction, quantity of allophanic constituents, and to relate these properties to nutrient element release and other soil properties. It is believed that the results of this study will provide basic information from which it would be possible to project other studies as a partial guide in conducting research work in soil-plant relations and to provide additional material for teaching about soils of Ethiopia.

PART II. LITERATURE REVIEW

Agriculture in Ethiopia

In the past, agriculture has played the role of a tap-root in Ethiopia's economic growth. Certain previous analytical results and empirical observations have indicated that agricultural development is a sine qua non for sustaining the self-sufficiency of the Country. Indeed, a recognition of this fact has gained new revival recently in that the Nation's Second Five Year Development Plan revealed that agricultural betterment will continue to command a priority for a long time in the future. In this connection, it is reported that currently agriculture accounts for about 70% of the share of the National income, and by a conservative estimate, about 90% of the population in Ethiopia is directly and indirectly engaged in this basic industry; what is more, this is predicted to continue for a considerable period in the future (25). The justification for the apparent over-emphasis of agriculture is sound, especially when one realizes that agricultural development is to play an additional role of a spring board toward industrialization.

Whereas food is a basic need for all human life, yet there is a serious shortage of this very substance on a global basis; and the twin problems of food shortage and population growth at a rate higher than food is made available are frighteningly obvious. However, the gravity of the hunger situation in all the world in general cannot go unchallenged if countries like Ethiopia would overhaul the management of their resources to the maximum in the light of modern information. Obviously

enough, Ethiopia is endowed with a combination of several favorable factors, such as potentially productive land with a considerably wider ratio of people to land and year-round climatic factors conducive to development. For the most part, saline-free water is adequately available in the Country, although not evenly distributed; there are numerous swamps which could be converted to watersheds, rivers characterized by permanency of flow, and lakes which could be utilized to advantage in irrigation. In addition to these, the heavy rains of the winter months could be conserved in order to be used in the relatively drier periods. By virtue of these facts alone, the Country is in a position favorable enough to contribute toward the alleviation of the problems of food shortage.

To maximize returns for agriculture in Ethiopia, therefore, it behooves real farmers to rely on at least four cardinal practices: (a) adequate irrigation, (b) emphasis of highest yield per gasha through fertilizer application, (c) initiation of erosion control at the farm level through cooperative schemes, and (d) mechanization. Traditionally, crop production in Ethiopia had been at the mercy of the heavy rains which last for about three months, although the benefits obtained from the intermittent "small rains" is also worthy of mention. Unfortunately, while rainwater is desirable, there is a concomitant complex of disadvantages associated with it; viz., the farmer finds it difficult to continue efficient work in the field under dashing rains when the rate of flood flow is at the highest, and loss from lodging is significant. During this season, also some insects and diseases tax the crops heavily. On the contrary, the remaining nine months which are ideal for irrigation practice are sunny and conducive to field work. There is very

little if anything to hinder the farmer from carrying on his work in the field. With sound fertilizer practice, it is possible to obtain not only two or more crops per year, but also the yield per production period can be augmented. These practices, coupled with erosion control, are the farmer's route to prosperity. As to mechanization, the ruggedness of the topography will decelerate some phases of this practice. This, along with expensive fuel and related factors, is indeed a challenge; however, some phases of mechanization can be practiced to advantage on selected areas of high returns and where productive factors are complementary to cash crops.

Certainly, in the annals of Ethiopian agriculture, the past is reminiscent of the limitations in technical "know-how," communications, transportation facilities, and related factors of production. These limitations have semi-paralyzed pertinent segments of the agricultural economy. With only traditional crude tools at his command, the native farmer has been able to manage the challenge of food shortage. Now that the Country has an up-to-date inventory of its assets in natural resources, systematic conservation and intelligent investment of these resources, geared to progressive development plans of other segments of the National economy, are advocated.

For Ethiopia's overall economic framework, excepting human life itself, probably no other resource excels in value the worth of the soils. Much has been already said on behalf of the fertility of these soils. The time is ripe to take quick steps to translate this into productivity. Naturally, a constantly high yield is possible from a land through long range conservation and wise management and utilization of the land; however, views exist that other acute problems commanding

priority of consideration prevail. Nevertheless, the salvation of the Country's economic future has its solace in the soils which are basic by all means. Hence, in the long run, a well-handled soil will complement the totality of the economy as planned. By the same token that production is power, a productive soil is the essence of the key to such power, at least in agriculture. Therefore, there is indeed a wisdom in bringing forward the cause of the soils of Ethiopia.

To this end, results of a broad general fertility survey have been reported recently (40, 41) and some data are available on the cation exchange capacity of some of the soils (13).

Geologic Information

According to Last and Mohr (35, 37) the continent of Africa, as well as the Deccan of India and the plateau of Brazil, is derived from the original continent of Gondawaland. The original continent according to them cracked at a later period, resulting in the division and drifting of the remnant blocks, of which the present continent of Africa is one. Metamorphic rocks consisting of crystalline material composed of granites and gneisses associated with valuable deposits of minerals constituted the base complex of the block of Africa; it is believed the formation of these earliest Ethiopian rocks took place during the Pre-Cambrian times, although actual age is unknown. According to Mohr (39), the Pre-Cambrian rocks in Africa are the largest sources of the mineral wealth of the continent. For the continent of Africa as a whole, deposits of sedimentary rocks are few. This is because the continental block remained above sea level for a considerably long period. Ethiopia happens to be one of these few areas in the continent that has sedimentary

deposits comprised of limestones and sandstones; later volcanic materials found in layers above the original crystalline rocks were added to these. Last (35) also points out that the oldest sedimentary rocks found in Ethiopia are likely to have been formed in the Triassic period at the time seas covered the eastern part of the region when the land dipped eastwards toward the present Indian Ocean; during Jurassic time, the Adigrat sandstones were assumed to have been deposited; with more depth, intensity and warmth of the seas, the Antalo limestones were formed; much more limestone and gypsum deposition took place in southern Ethiopia during the Cretaceous period, and the last sedimentary rocks (small in areal extent) were deposited at the end of the Miocene period, subsequent to which the whole region was uplifted in a dome formation which extended over the whole of present Ethiopia. This entailed the present site of Addis Ababa at about the center of the dome.

Last's account (35) also has it that the Abbay River area in the vicinity of the bridge is a classic illustration of certain areas which have been eroded with a resultant exposure of the original rock.

Subsequent to the formation of the African physical block, the phenomenon of block faulting occurred which produced cracks along the eastern side of the continent. This resulted in the Rift Valley structures which extend from Mozambique to the Middle-East, passing through Ethiopia. Also, volcanic activity accompanied the faulting, and thus, great thickness of lava, now referred to as plateau basalts gushed on to the surface of the earth via fissures and through immense volcanoes. At present these plateau basalts prevalent in various sections of Africa underlie the great tablelands of the Ethiopian western plateaus and the exceedingly eroded remnants of the eastern highlands stretching from

Sidamo to Harargai. Existing evidence that the volcanic activity has left its impression in the land is reflected by the active cones in the Danakil region and by the hot springs which appear in certain parts of the rest of the Country.

The floor of the Rift Valley structure contains a number of lakes, including lakes Nyasa, Tanganyika, Edward, Albert, and Rudolf; in Ethiopia, lakes Ziway, Langano, Abiata, Awasa, Shala, and Abaya are also situated in these troughs of the Rift Valley. Being situated in enclosed basins, these lakes are part of the inland drainage. The Tertiary period is identified with geological phenomena which effected the small active volcanic cones in the Afar region, hot springs were scattered over the Country, and volcanoes of recent activity, though now dormant; e.g., Fentalle, Musa Ali Afdera, and Chubbi near Shashemané. Included also in this igneous activity are surface deposits of recent lava from fissures in the Rift Valley and the Danakil region, and earth tremors, landslides and earthquakes are still recorded in the area. An average of seven local tremors per month is recorded in Addis Ababa (35).

The formation of small local ice caps in the highlands in Ethiopia during the Ice Ages or Pluvial Period is reported as shown by smooth rocks, moraines, etc., in several regions and other evidence of glaciation in such regions as the Semien Mountain (35).

During this Pluvial Period, erosion was severe, and the cutting of the great gorges in the plateau lands was accelerated. Rejuvenation of the river courses along with the continued uplift of the plateau gave way to deposition of alluvium and gravel around the margins of the highlands. Since the climate of Africa was known to have been less drier in the Pleistone Period than it currently is, the Great Rift lakes reached

their maximum size during the Pluvial Period. Geologists assume that at this period lakes Abbaya and Chamo were united and the four northerly lakes: Zway, Langano, Abiyata, and Shala comprised a single sheet of water. Subsequent to drying of these lakes, sedimentary deposits including salts and other minerals were precipitated (35, 39).

As to the river systems and drainage in Ethiopia, the uplifting of the Ethiopian region during the Tertiary period is believed to be the cause for the general drainage pattern. Cracks emerged at the center of the dome due to faulting, and the region therefore appears crossed from north to south by a rift valley. Extensive highland area, retaining to the east and west the original slopes of the dome, appear on both sides of the valley; generally, the western highlands slope toward the Sudan and the eastern highlands slope toward the Indian Ocean. As a result of the fault lines marking the boundaries of the Rift Valley, two watersheds appeared: one major watershed separates the drainage westwards toward the Sudan from the drainage eastwards into the Rift Valley. The western plateaus and southwest highlands are the main regions of high rainfall, and the westward flowing rivers are therefore responsible for a high proportion of the water drainage from Ethiopia. In order of total annual volume the major rivers rank as follows: Abay > Tekezze = Angereb > Baro = Akobo > Omo > Wabie-Sebele > Ganale = Gestro > Dawa > Awash Mereb = Gash > Barka > Sagan. The River Sagan flows to Chew-Bahr. The first three are rivers which flow westwards to form part of the Nile drainage basin and, as such, represent about one-half of the water outflow from Ethiopia, although the catchment area of these three rivers is reported to total only one-quarter of the Country's total area. The southwest highlands are drained by the left-bank tributaries of the Abay, the Baro-Akobo

River system and the Ghibbe-Omo River system. These southwest highlands are in a much more advanced stage of erosion than the northern plateaus.

Clay Mineral Studies

Type of clay minerals occurring in soils are estimated by various methods. Generally, the main series of clay minerals include the montmorillonites, kaolinite, illite, or hydrous mica.

The montmorillonite series consist of saponite, beidellite, nontronite, and montmorillonite proper. In saponite all of the aluminum is replaced by magnesium; in nontronite a fraction of the aluminum of the gibbsite layer is replaced by iron; in beidellite, a higher aluminum and a lower silicon content occurs, and this is suggestive of the fact that in the silicon tetrahedral sheets, replacement of some Si^{+4} by Al^{+3} is possible. Montmorillonite proper, on the contrary, is of the chemical composition $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot \text{X H}_2\text{O}$ with the usual presence of magnesium. This mineral consists of structural units possessing a gibbsite sheet between two sheets of tetrahedral silica groups; and these structural units are loosely held together by the H_2O molecules usually occurring between them (47, 49, 55).

The kaolinite series includes dickite, nacrite, anauxite, and kaolinite proper, which is the most common of the group and is of the composition $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$ (55). The structural unit of kaolinite is such that it consists of a double sheet composed of one gibbsite layer, which exhibits aluminum in octahedral coordination and one Si-O layer consisting of silica in tetrahedral coordination.

Compositions of dickite and nacrite are similar to that of kaolinite, but they differ from kaolinite in crystallographic forms (55).

Halloysite is reported to be closely related to kaolinite; however, it has been shown that it has a distinct X-ray pattern and a dehydration curve (47, 49, 55).

Illite is of the composition $K Al_2 A Si_3 O_{10} (OH)_2 \cdot X H_2O$ and is similar to montmorillonite; since, like montmorillonite, it is composed of a gibbsite sheet between two sheets of tetrahedral silica groups, its structure is considered to be intermediate between muscovite and montmorillonite.

Since potassium is the interlayer ion that forms a strong bridge between the Si-O layers it is known to have a tendency to prevent adsorption of water and to limit the base exchange capacity of the interlayer ions (55).

Techniques which have been employed in the past for proper identification and classification of clay minerals were variable (44, 49, 50, 55). Those most commonly used included differential thermal analysis, dehydration curves, optical and electron microscopy, X-ray diffraction analysis, and cation exchange capacity determinations. The optical method consists of the use of refractive indices and is not particularly suited to soil colloids; the indices represent an average for a mixture of clay minerals commonly found in the soil. Differential thermal analysis deals with detection of the endothermic and exothermic reactions of clay minerals during a process of gradual heating. As each clay mineral is known for its characteristic thermal curve, comparing the intensity of the thermal "pips" with known standards of clay mineral mixtures gives quantitative estimation of the clay mineral; upon heating there is an exclusion of chemically bound water in the clay lattice. The X-ray analysis technique is regarded as the most accurate method of clay

mineral identification, regardless of the difficulty encountered in differentiating illite or hydrous mica diffraction patterns from those of montmorillonite.

Dyal and Hendricks (14) adopted ethylene glycol retention technique which is essentially a gravimetric method for the measurement of total and external surfaces and, by difference, for internal clay surface determination on the basis of the clay ethylene glycol retention.

Kelly (31) reports of the wide use of cation exchange capacity in the quantitative estimation of clay minerals. Under suitable conditions, clay minerals can adsorb cations, and these cations are exchangeable with other cations. In this connection, it is known that illite and montmorillonite have similar exchange capacity mechanisms (55). The base exchange capacity in montmorillonite is high because of ion replacement within the lattice. Replacement of Al^{+3} by Mg^{+2} occurs in the gibbsite layer, and this entails an excess negative charge on the lattice; almost twenty percent of the Al^{+3} position is replaced by Mg^{+2} in the gibbsite layer which corresponds to a base exchange capacity of approximately 100 m. e. per 100 grams; also Al^{+3} can replace Si^{+4} in the tetrahedral sheets, but this replacement is not appreciably significant in the montmorillonite series (55). Montmorillonite consists of loosely held units; it can markedly expand when wet--exhibiting an enormous surface area for adsorbing exchangeable cations. Part of the exchange capacity montmorillonite possesses is attributed to broken bonds at the end of the colloidal fragments (31, 55).

Houser and Reed (23) hold that montmorillonite particle size varies with the degree of dispersion and separation of all montmorillonite particles into plates of unit thickness resulting subsequent to

ultimate dispersion; however, base exchange capacity of montmorillonite is independent of particle size. In illite, about 15 percent of the Si^{+4} is replaced by Al^{+3} than is the case in montmorillonite. Potassium ions satisfy the excess charge resulting from such replacement, and there is limited expansion between the units. This, coupled with the binding together following agitation with water, minimizes the surface area available for base exchange in illitic clay minerals, according to information presented by Grim (20).

According to Kelly (31), since kaolinitic lattice charges are satisfied internally, kaolinite is incapable of cation attraction save by negative charges resulting from the broken bonds on the edges of the mineral fragment.

Gieseking (19) maintains that inorganic exchange capacity may range from virtually nil to 60 milliequivalents per 100 grams of soils.

Kelly (31) on the other hand reports that soils high in montmorillonite have base exchange rarely in excess of 75 milliequivalents per 100 grams of colloid; and Ross and Hendricks (48) hold that all montmorillonite type minerals have about the same magnitude of base exchange capacity, normally about 85 milliequivalents per 100 grams. Some variation in base exchange capacity is attributed to degree of weathering and error of omission; viz., certain soil colloids consist of uncombined oxides and hydroxides, as well as colloidal silicon, according to some investigators (46, 47, 51).

The role of potassium in the estimation of clay minerals is particularly interesting. It is estimated that there is about 6% of K_2O in illite (51), and the potassium content of soils is regarded to be a good index for the estimation of illite. According to Kelly (31),

since potassium of hydrous mica varies in magnitude with variation of source, it can be used only for a rough estimation of the mineral.

Alexander, et al., (1), maintain, however, that since illite is the only mineral containing potassium, the latter is a good criterion for estimating the former. The validity of this view gets support by other workers (7, 8, 10, 12) who are of the view that colloids which contain in excess of one percent K_2O indicate that the predominant mineral in the colloids is illite; that potassium can be held in two forms other than illite, namely, muscovite and fixed potassium in montmorillonite, is also indicated by Jackson and Hellman (27) and that the amount of potassium fixable in montmorillonite in a non-exchangeable form is known to range from 0.7 to 0.9 percent.

Several workers (38, 51, 55) have reported that the content of K_2O in illite ranges from 5 to 6 percent.

Allophanes vs. Delta Values

Reports by several investigators (2, 26, 45, 55) have indicated that allophanes and allophanic clays exhibit significant variation in the magnitude of cation exchange capacity values. It was demonstrated that clay separated from Ando soils in a pH 3.5 dispersion medium was about one-third as high in cation exchange capacity as clay separates from an alkaline medium of pH 10.5. It was also possible to obtain more cation exchange capacity by re-treating the acid clay separates with mildly alkaline buffer. The difference of the cation exchange capacity in clay separates according to the pH of the dispersion reagents used for separation is termed the cation exchange delta value. This value is used for the quantitative determination of the allophane

content of soils of volcanic ash origin.

Aomine and Jackson (22) conducted successive treatments of Ando soils with 2% Na_2CO_3 solution of pH 10.5 and 1 N NaOAc buffer of various pH values and studied the effects these had on cation exchange capacity; they observed a decrease of cation exchange capacity by acid treatment and attributed this decrease to replacement of the sodium ions by non-replaceable H-ions through OH formation and dissolution of the colloid or non-reversibility (2). The reports of these investigators included also the finding that the cation exchange delta value was significantly high in the Ando (2, 4, 5, 6, 45) allophanes, and is appreciable in montmorillonite and halloysite, and negligible in kaolinite, gibbsite, and quartz. Vermiculite was assumed to have as much delta exchange as that of montmorillonite; and illite and chlorite are estimated to have about one-half of the cation exchange capacity delta values as those of montmorillonite.

The cation exchange capacity delta values of allophane and of various crystalline clay minerals shown in Table I were adapted from information presented by Jackson (26).

In this connection it was pointed out by Jackson (26) that the delta value for the sample, allocated to the respective mineral as shown in Table I gives a satisfactory analysis, consistent with X-ray diffraction, differential thermal analysis, and other data.

Birrell and Fields (5) have shown that the physical properties of allophanic volcanic ash include high water-holding capacity, high shrinkage, irreversible drying, and moderately high compressibility under load. The parent material which is partially responsible for imparting the properties listed above consists of water-sorted volcanic ash. The

TABLE I
CATION EXCHANGE DELTA VALUES OF ALLOPHANE AND
VARIOUS CRYSTALLINE CLAY MINERALS (26)

	meq. per 100 gms
Allophane	100
Halloysite	18
Montmorillonite	10
Vermiculite	10
Illite	5
Chlorite	5
Kaolinite, Gibbsite, or Quartz	0

clay fraction is fairly pure allophane which is virtually free of sesquioxides. It was also reported by these investigators that through the use of an X-ray diffractometer, the predominance of allophane in the clay fractions in some volcanic ash soils was inferred from the amorphous nature of the material. The X-ray amorphous character of the clay was shown by lack of diffraction and particle size below 100\AA . Reference is also made to Ross and Kerr's report that the silica-alumina ratios for allophane range from 0.74 to 1.98 (5).

The base exchange capacity of allophane (51) is known to be basically low; however, treatment with alkali tartrates or oxalates would produce high alkali content in these clays. The capacity of allophane to take up excess quantities of alkali metals was confirmed by leaching the deferrated clay and silt fractions with a neutral potassium acetate solution, and removing excess salt with alcohol and the subsequent determination of potassium leached out of the soil by ammonium acetate solution.

According to Birrell and Fields (5) the alkali metals in deferrated allophanic clays appear more loosely held than are the exchangeable bases held by other clay minerals. The dye adsorptive power of ignited allophane is reported to be about 70 percent of that of ignited gibbsite. Such dye sorption is used for determining the gibbsite content of clay minerals; these investigators recommend that this procedure should be used with caution when allophane is known to be present.

Reference was made to previous suggestions that $1/500$ NH_4Cl should be used as a dispersant for volcanic ash soils which contain allophane and sesquioxides. It is also pointed out that the isoelectric point of allophane is slightly on the acid side of neutrality (5, 26). It has

been found that allophane is the primary mineral in the clay fractions of soils found in New Zealand originating from andesitic and rhyolitic volcanic ash showers, and the allophane has been shown to be commonly responsible for the characteristic physical properties of the andesitic ash soils. The chemical composition variation follows that of the geologic specimens described by other investigators; and deferration pretreatment of the soil before the separation of clay minerals entails loss of alumina (5).

Potassium Studies

Ramamoorthy and Paliwal (43) reported that Nelson, et al., noted that there are limitations in comparing many soil test methods on different types of soils for judging the availability of soil potassium in order to evaluate crop need of potassic fertilizers. These limitations are known to be due to heterogeneity of soil population which is partly due to the differing colloidal characteristics of the various soils. It is known that the movement of an exchangeable cation from the exchange complex will depend on the ratio of the activities of the ions concerned. Schofield (52) defined this as the Ratio Law, which in effect means that when cations in a dilute solution are in equilibrium with the cations in the exchangeable phase, a change in activity of the ions in solution will not disturb the equilibrium if the activities of all the monovalent ions are changed in the same ratio, those of the divalent ions in the square of the ratio, and those of the trivalent ions in the cube of that ratio. The application of the Donnan membrane equilibrium conditions to the distribution of ions between cations on the exchange complex and the solution phase of the colloid-water system gives the

same result as obtained by the Ratio Law.

Thus, the free energy change involved in the exchange of potassium by an equivalent amount of calcium at a temperature T is expressed by the following relation (45):

$$F = -RT \ln (a_K/a_{Ca}^{1/2}).$$

Here, no serious error is involved by assuming that magnesium behaves like calcium. The above expression is modified further:

$$F = -RT \ln \frac{a_K}{(a_{Ca} + a_{Mg})^{1/2}} = RTp \text{ K.A.R. where K.A.R. refers to}$$

potassium adsorption ratio, F = free energy, a_{Ca} = activity of calcium, a_{Mg} = activity of magnesium, a_K = activity of potassium, R = Universal gas constant, and T = temperature in $^{\circ}K$.

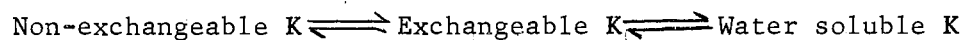
Ramamoorthy and Paliwal (45) further studied the comparison of the equilibrium potassium adsorption ratio of soils with conventional soil tests in respect to their correlation with response of paddy to potassic fertilization on very heterogeneous soils. They found that the potassium adsorption ratio calculated correlated with crop responses significantly at the 1 percent level for the soils separately and for all soils, except for one where the significance was at the 2 percent level. None of the different methods studied correlated significantly for all the plots separately. They generalized on this basis that the equilibrium potassium adsorption ratio of soils calculated by the rapid method seems to have a wider applicability in soils of very heterogeneous nature; and the equilibrium potassium adsorption ratio of plants seemed to determine the limit of the potassium adsorption ratio of the soil up to which potash fertilization of crops will be useful (45).

Garman's studies (18) of potassium release by continuous cropping

indicated that significant deviation from the average uptake by each of five successive crops consisting of Romaine lettuce, corn, rape, and sudan grass, was greater among Gray Brown than among the Brown Podzolic or Podzol soils. He found that the potassium release to crops was in the order of: Brown Forest > Gray-Brown Podzolic > Brown Podzolic > Podzol, for both surface and subsoils. The subsoils did not release as much potassium as did their upper surface horizons. Garman (18) holds that the continuous cropping of soils seems to result in a good index for rating soils as to their relative potassium supplying ability. His data indicated that most of the easily replaceable potassium is removed by the first crop under the intensive conditions established by pot culture. The second, third, and successive crops take it up at a lesser but rather uniform rate, until other factors become limiting. Chemical methods are reported to give better results at times according to this worker (18) than do plants grown in pot cultures. This is due to the reasons that physical restrictions on root development by poor soil structural conditions, climatic environment, rate and method of watering, and the availability of other elements govern the plant uptake of specific nutrient elements. These physical and biological factors are not likely to control the removal of an element by a chemical method. It remains, however, that the standard for determining the availability and release of mineral nutrient elements is crop removal. The continuous leaching method with 0.01 N HCl solution was developed for the characterization of significant differences between soils and groups of soils.

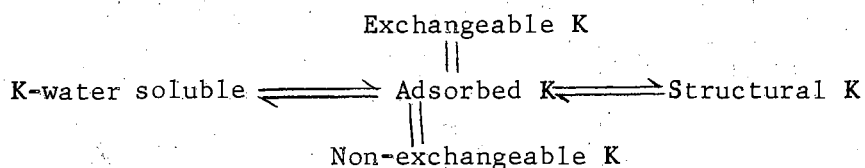
Several workers have considered the concept of equilibrium between the different forms of soil potassium. Hissink (22) proposed this basic

concept earlier; Peech and Bradfield (43) showed a schematic arrangement as appears below:



Exchangeable potassium refers to the quantity removed with a definite extractant of specific concentration and dilution ratio, and hence, it is not regarded as a true characteristic of the soil.

The accepted view is that "exchangeable potassium" is adsorbed on the surface of soil particles. Other views maintain that all "adsorbed potassium" is synonymous with "exchangeable potassium." It is suggested also that "non-exchangeable potassium" may include strongly sorbed potassium. Garman (18) therefore presents the following argument as a more meaningful description of the equilibrium condition of the various forms of soil potassium:



Garman advocates further that this arrangement allows for a more precise interpretation of the potassium status in the soil. Accordingly, "adsorbed potassium" is defined as that fraction which is held electrostatically by excess negative charges on the surface of clay mineral particles (or by the organic matter) and is replaceable by other cations without altering the nature of the exchange material; the usual ammonium acetate extraction is known not to remove all of it on account that differences in location, accessibility, and bonding energy of the adsorbed potassium are governing factors. Hence, the fraction

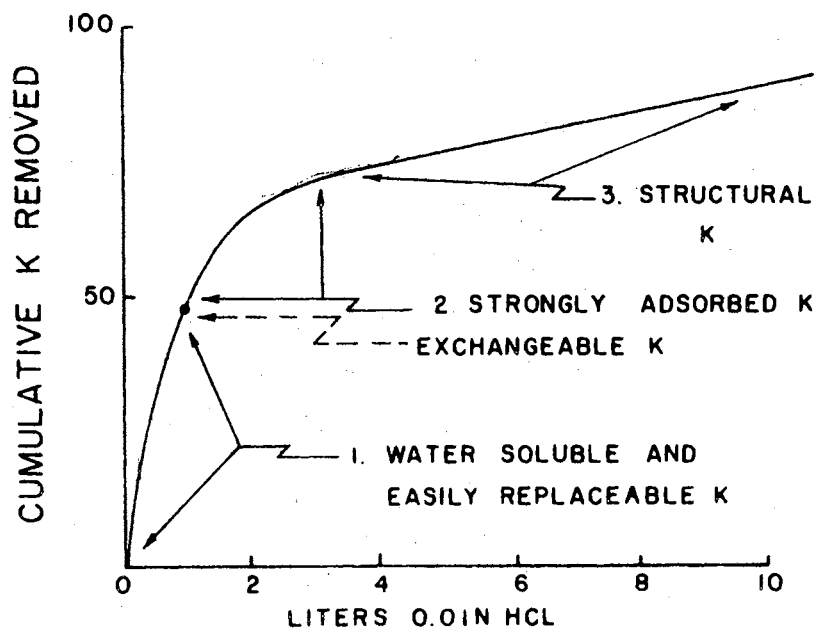


Figure 1. An idealized characteristic potassium release curve of soil leached with 0.01 N HCl, (18).

referred to as "non-exchangeable" may include both "strongly adsorbed" and "structural potassium." There is a difference in the ease of replacement of these two forms, and therefore, they are categorized separately. Structural potassium is thus the fraction of the soil potassium which is combined in the crystal structure of both the primary and the secondary minerals. As such, it is considered to function in the equilibrium equation and plays the specific role of "Reserve" supply for the maintenance of constancy of potassium relationships in the soil; however, it is not readily replaced by other cations in most extracting solutions. When potassium is supplied to the soil it becomes "fixed" as "structural potassium" in either the primary or secondary mineral form.

The release rate of potassium is a direct function of pH and that the order of effectiveness of different ions to replace potassium was $H^+ > Na^+ > Li^+ > Ca^{++} > Mg^{++} > NH^+$. It was further demonstrated that the release rate substantially increased above exchangeable level at pH values less than 3.0. Garman's investigation also substantiated this information.

PART III. MATERIALS AND METHODS

The soil samples used in this study were collected from five different locations in Ethiopia. Permission for entering them into the United States was granted by the United States Department of Agriculture, Plant Quarantine Division. After the arrival of the samples in the United States, they were processed and made ready for the various analyses undertaken in this study.

Description of the Soils

Dark (blackland) clay soils

In this study the blackland soils are represented by samples obtained from the Sembel farm in Eritrea, those collected in Debre-Zeit, Yerer Gota, and the Agricultural College Blackland Experiment Station in Harargai. These soils are found on rolling to level topography, ranging from good to poor in surface drainage and moderate to slow internal drainage. The climax vegetation consists of short to tall grasses, and under cultivation small grains including *Erogrostis téf* are grown. Some drought-tolerant woody plants (41) including Acacia and Juniperus Procera are widely spread. Eucalyptus planted in the environs of Addis Ababa and other cities grows abundantly. All of these and related species of trees are normally found on vertisols. The texture of these soils ranges from clay loam to silty clay. The dark color of the soils is partially due to the nature of the parent material (40), which is basaltic rock, for the most part; it is also known that

some limestone is scattered over certain localities. The dark color is also attributed to the types of humification; however, the amount of organic matter might be a contributing factor to a certain degree. Subsequent to water-logging during the rainy season, these soils swell; and upon drought they shrink, ultimately forming wide cracks. When wet they are sticky and plastic and upon dessication, they exhibit granularity. The apparent characteristic swelling when wet and the wide open cracks following dessication during which time self-mulching and crumbling are noted, as well as the high cation exchange capacity previously reported (13, 40) have strongly suggested, along with the results of related observations (40), that these soils could be inferred to be of montmorillonitic clay mineral nature. The present study has substantiated this view.

Studies heretofore have indicated that generally the profiles of these soils are deep and that the clay content is high, averaging more than 60 percent, throughout the entire profile. The subsurface is angular blocky associated with slickensides to almost massive (41). Previous studies (40) have also shown that in certain cases calcium concretions are known to occur on the surface and throughout the entire profile; these soils have pH values ranging from 5 to 8, although they usually range slightly acid to slightly alkaline.

The following is a typical profile description of the blackland soils, as previously presented (13).

0-12 inches--very dark gray clay, granular surface, sub-angular blocky below
12-42 inches--very dark clay to black clay, appearing massive but breaks to subangular blocks

42-60 inches--very dark grayish brown to very dark gray clay, some CaCO_3 concretions, subangular blocky.

For further details on individual profiles, refer to (13) and to Murphy's reports (40, 41).

Since shrinkage, shearing, and wide cracks are characteristic of vertisols, and since the other descriptions which fit vertisols are significantly identified with many blackland soils of the Ethiopian highlands, these soils are considered as vertisols (40, 54). Indeed, in Ethiopia where these soils occur, it is not uncommon for fences and telephone poles to be thrown out of line and for trees and certain buildings to tilt, for pavements to be broken or shifted laterally, and for foundations of buildings to be affected unless deeply laid. Gullying is also prevalent. Such are the various effects of the mass movements which are true of vertisols; and it becomes apparent, therefore, that the blackland soils under study are vertisols, according to the Seventh Approximation soil classification scheme (54). Although in certain cases these soils may be categorized under the Mazaquert great soil group, generally they belong to the Grumaquert great soil group; the suborder is Aquert, thus they are Grumosols (13, 40, 41, 54).

Studies of the texture (40) and organic matter content of the soils under consideration are presented in Table II. The organic matter content for these soils ranges from a low of 1.3 to a high of 5.0 percent, with an average of about 3.22 percent. The mechanical analysis showed that all of these soils were high in clay.

Reddish Brown Soils

Detailed descriptions of these soils are found elsewhere (13, 40,

TABLE II
 TEXTURE (40) AND PERCENT ORGANIC MATTER
 FOR BLACKLAND AND REDDISH BROWN SOILS

Sample Number	Mechanical Analysis				
	% o.m.	% Silt	% Silt	% Clay	% Colloidal Clay
DZ-1	2.4	9.0	37.0	54.0	-
DZ-5	1.3	11.0	21.0	68.0	-
DZ-9	3.7	5.0	24.0	71.0	-
DZ-13	2.8	3.0	18.0	79.0	-
J-17	5.0	22.6	34.4	43.0	28.8
J-22	4.6	23.6	35.4	41.0	27.8
CB-27	3.9	15.4	22.0	62.6	33.0
CB-32	4.2	14.4	20.0	65.6	42.0
YG-37	2.8	34.4	18.0	51.6	28.0
YG-40	2.0	26.4	18.0	55.6	33.0
A-44	3.0	15.5	22.0	62.5	-
A-47	2.9	15.5	22.0	62.5	-

41, 54). For the most part these soils occur on gentle to steep slopes, and are especially dominant on steep slopes. They fit very well the descriptions given for the order "Oxisols" (54). Oxisols are otherwise known as Latosols and Ground Water Laterites. Sometimes the word "Laterite" has been used to denote this group of soils. The term Oxisols refers generally to all the soils possessing oxic horizons whose epipedons may be umbric or orchic, histic, and possibly mollic. According to the Seventh Approximation, (54), the occurrence of this group of soils is restricted to tropical and subtropical regions; usually these soils have argillic horizons and often occupy old land surfaces.

Profile studies of this order of soils in various parts of Ethiopia were conducted in the past, and it was shown that on the whole, the soils of the west and southwest, where there is high rainfall, are acid throughout the profile. They are also low in calcium saturation and available phosphorus, moderate to strong in structure with coarse granular surface soils, firm, moderately coarse subangular blocky in the subsurface where the clay content is higher than at the surface. For instance, the Jimma-Saka soils are characterized by the low calcium saturation and exchangeable potassium content; they have been demonstrated to be loamy in texture, although mechanical analysis studies have shown that they are clay loams to clays. The Fedis soils in Harargai and a few others which are under low rainfall are of neutral pH, have an exchange complex saturated with bases, primarily calcium, and are lower in nitrogen and organic matter than the acid soils and are considered, therefore, to be young soils. The profile studies of the Wonji soils (Reddish Brown) in the Awash Valley near Nazareth are known to range from sandy loam to clay in texture, have a high degree

of calcium saturation, and are high in available phosphorus.

Most of these profiles have percent cation saturation of the exchange complex which range from as low as 39 percent to about 77 percent.

The following is a description of a profile of a virgin soil near Jimma (13).

0-10 inches--35 percent sand, 20 percent silt, 45 percent clay; 5YR 4/4; granular, pH 5.6.

10-24 inches--21 percent sand, 18 percent silt, 61 percent clay; 5YR 4/6; horizontal cracks, pH 5.7.

24-42 inches--12 percent sand, 8 percent silt, 80 percent clay; 5YR 4/6; vertical cracks, pH 6.0.

60 inches † (undetermined) --27 percent sand, 14 percent silt, 59 percent clay; concretionary zone; 5YR 5/6; pH 6.2.

For the profile described above, the color was dark reddish brown when moist. For the horizons, the organic matter content was 5.20 percent for the surface horizon, 2.35 percent, 1.25 percent, and 0.25 percent for the 60 inches † depth. For further details on individual profiles, refer to (13) and to Murphy's reports (40, 41).

Roots of plants penetrate all the profiles quite well. The water holding capacity, and both surface and internal drainage of these profiles are good. The profiles are thus deep and permeable, adsorbing water readily. Although they show stickiness when moistened, the surface of the soil dries rapidly to a desirable, friable structure. Kaolinite along with some montmorillonite is the likely dominant clay mineral, both according to previous observations (13, 40, 41) and to supporting data gathered in the present study. Previous reports that the organic matter is high in these soils ranging from 3 to 8 percent

in the plow zone and that the pH is 5.0 to 6.0 is substantiated in the current study.

Methods Employed

Potassium release. Potassium release was determined by using Garman's procedure (18) for qualitatively separating the easily exchangeable, strongly adsorbed or exchangeable potassium, and structural potassium. Essentially, twenty-five grams of twenty mesh air dry soils were mixed with an equal volume of 20 mesh acid-washed quartz sand and placed in a six-inch leaching tube and plugged with a cotton filter. The leaching tube was fitted into a sinter glass plugged leaching column 10 inches long by 0.5 inch wide that was filled with an acid (H) saturated IRA-120H amberlite resin. The resin tube was saturated with the leaching solution at all times and the stopcock closed except during the leaching procedure. The leaching tube was filled 2/3 full of leaching solution before the soil sand mixture was introduced. The resin column was then fitted into a 50 liter bottle (for twenty-four sample leachings, concomittantly). A glass manifold was placed on top of the leaching rack and connected to the 50 liter bottle which was placed higher than the manifold; the latter was connected to tubes which delivered continuous leaching solution to the funnels containing the samples. Thus, leaching with 0.01 N HCl was carried out. Subsequently, the potassium was removed from the resin tube after each liter of leaching solution moved through the soil. The rate of leaching was about one liter per six hours. The potassium removed and held by the resin was collected by washing the resin column with 10 percent HCl acid. The washing also regenerated the resin for the next leaching

procedure. Potassium was determined on each leaching on the flame spectrophotometer. The data are presented in tabular and graphic form. Data obtained on calcium, magnesium, and sodium were also presented in tabular forms and included in the appendix. The quantity of potassium removed is correlated with presence or absence of allophanic type soils.

Allophane. To determine the allophane content two five-gram samples of soil were taken from each representative soil sample and washed twice with 1 N sodium acetate buffer of pH 5.0 in 100 ml centrifuge tubes to remove exchangeable calcium; then the samples were treated with 30% hydrogen peroxide several times in 250 ml beakers to remove organic matter. The two samples were washed with acetone by means of the centrifuge in 100 ml centrifuge tubes. One sample #A was transferred to a porcelain dish, dried at 105°C, weighed, and reported as total mineral matter. Sample #B was given the iron oxide removal treatment which involved a digestion with sodium dithionite, sodium citrate and sodium bicarbonate, and the free iron was determined by the Tiron method (26). At this point 10 ml of acetone was added to the soil suspension to insure obtaining a clear supernatant solution. The soil residue in the tube was washed successively with 50, 75, and 100% acetone, then transferred to a 400 ml nickel beaker with 200 ml of water. Four grams of sodium carbonate was added, the solution stirred thoroughly and covered with a watch glass and boiled for five minutes. The soil suspension was centrifuged until clear, the supernatant discarded, and the residue was washed twice with 50% acetone, then with 75% acetone, and then with 100% acetone. After the final washing and centrifugation the sample was washed into a weighed porcelain dish and dried at 105°C.

Dissolved Allophane = (sample A in gms) - (sample B in gms) -

$$\frac{\text{Extracted Fe}_2\text{O}_3}{.85}$$

where .85 represents the

hydration of limonite.

Delta Value. To determine the delta value 0.8 gram samples were taken from sample #B (the sample treated with dithionite and boiling sodium carbonate) and weighed into two 15 ml centrifuge tubes; then 5 ml of 1 N pH 3.5 sodium acetate buffer was added to one tube and 5 ml of 2% sodium carbonate solution was introduced into the other tube. The tubes were placed in a boiling water bath and agitated intermittently; the pH 3.5 tubes were boiled for 15 minutes and the sodium carbonate tubes were boiled for 60 minutes. The solids were centrifuged out, supernatant solution discarded, and the samples washed five times with 1 N pH 7 sodium acetate and was determined by the flame method. In all washings in the 15 ml tubes about 10 ml of solution was used for washing. The difference between the two cation exchange capacity values is referred to as the cation exchange capacity delta value.

Interlayer and exchangeable aluminum (27). Interlayer and exchangeable aluminum was extracted from 1 gram soil samples with organic matter present and with organic matter removed by hydrogen peroxide treatment. The removal procedure consisted of extraction with 10 ml of the extraction mixture. Aluminum was determined by the aluminon procedure (26). The quantity of aluminum extracted was correlated with clay content, soil organic matter, and an empirical estimation of granularity.

Organic matter (40). Organic matter was determined by employing

potassium dichromate in which one-half gram of 20 mesh soil was treated with 10 ml of 0.4 normal potassium dichromate and 15 ml of concentrated sulfuric acid, in a 200 ml tall beaker. After heating to about 165°C with a concomittant shaking, 100 ml distilled water was added, the solution allowed to cool, and 4 drops of ortho-phenanthroline was added. The solution was then treated with standard ferrous ammonium sulfate (FAS) to a reddish tinge using a light box to sharpen the end point (26).

$$\text{Normality of FAS} = \frac{N \text{ of } K_2Cr_2O_7 \times \text{ml } K_2Cr_2O_7}{\text{ml FAS in blank}}$$

As 0.5 gram samples were used, the calculation was carried out as follows:

$$(\text{Blank} - \text{ml FAS}) \quad (\text{Normality FAS}) \quad (1.25) = \% \text{ organic matter.}$$

Texture. Soil texture was determined by Bouyoucos method and where this was not possible, it was done by feel (40).

pH. Soil reaction was determined by using soil paste and distilled water and a Beckman Zeromatic pH-meter was employed for reading the pH, (40).

Cation exchange capacity was calculated as follows:

Since the volume of the total extract per sample was 50 ml out of which 10 ml was used, and normality of EDTA was 0.0106 and that the amount of sample used was 0.8 gm, $.0106 \times \frac{100}{0.08} \times \text{ml EDTA used times}$
 $\frac{50 \text{ ml extract}}{10 \text{ ml of the extract used}}$ gave the CEC in ml per 100 gm soils (40).

PART IV. RESULTS AND DISCUSSIONS

Cation Exchange Capacity Delta Values

Where 2% Na_2CO_3 was used, the cation exchange capacities for the samples analyzed varied from 27.49 to 63.00 milliequivalents. The average cation exchange capacity for the Jimma soils was 44.55 milliequivalents per 100 grams of soils, a value slightly higher than some previous findings (13). In general, for the blackland soils the average was close to 52.50 milliequivalents per 100 grams, although some individual samples were higher.

Where 1 N pH 3.5 CH_3COONa was used, the average cation exchange capacity for the Jimma soils was about 38.26, which were higher values than those reported previously (13). For the College Blackland Experiment Station Farm, Asmara, Debre-Zeit, and Yerer Gota dark soils, the average cation exchange capacity obtained by this method was about 45.25 milliequivalents/100 grams.

Thus, the cation exchange capacities were higher for the dark soils than for the Jimma oxisols by both methods; however, no significant difference in these values was observed either among samples within the vertisols, between samples within the oxisols, or between the vertisols and oxisols. Interestingly enough, no significant difference was obtained in values by using the different methods of cation exchange capacity. This is contrary to data that are normally obtained for allophanic soils; therefore, it might be concluded that

these soils are not allophanic.

The delta values calculated for all the samples under study were low. The indication was that these soils were not allophanic, at least not significantly so. Jackson (26) reported that allophanic soils should have delta values of 100 m.e. per 100 grams of the soil and that soils with other clay minerals have values less than these (see Table I).

That there are only trace quantities of allophane in the Ethiopian soils studied was also confirmed by the low percentage of these minerals calculated for the samples (Table IV). Based on the information presented by Jackson (26) and also the comparison made between the results obtained here and Jackson's data, it might be concluded that the dark soils of the College Blackland Experiment Station Farm, the Debre-Zeit Experiment Station, the Yerer Gota Fruit Farm, and the Sembel farm in Eritrea were dominantly montmorillonitic. Those samples from the Jimma area were kaolinitic, according to these findings.

Statistical analysis indicated that there was no correlation between the delta values and the interlayer aluminum; also, there was no correlation between the interlayer aluminum and potassium released subsequent to the first liter of leaching with 0.01 N HCl.

None of the samples studied had dissolved allophane in excess of that known to normally occur in soils of montmorillonitic clays. The data obtained for allophane clay content are indicated in Table IV.

The potassium study results are present in Tables VI and VII. The family of curves obtained by replicate determinations consistently followed the idealized curve reported by Garman (Figure 1) (18).

The Debre-Zeit samples (Figure 2) showed significant variation

TABLE III
 CATION EXCHANGE CAPACITY DELTA VALUES FOR
 THE DARK AND REDDISH BROWN SOILS

Sample Number	(A) CEC Determined with 1 N pH 3.5 CH_3COONa	(B) CEC Determined with 2% Na_2CO_3	Delta Value
	Average Value	Average Value	
DZ-1	48.68	39.09	8.61
DZ-5	46.38	38.10	7.94
DZ-9	28.49	27.49	1.99
DZ-13	28.49	38.10	9.93
J-17	47.37	36.44	9.94
J-22	29.15	34.39	5.24
CB-27	48.36	56.30	7.94
CB-32	48.36	56.36	8.00
YG-37	56.31	50.35	6.04
YG-40	48.69	56.30	7.61
A-44	66.25	60.95	5.30
A-47	56.31	63.00	6.69

TABLE IV
 QUANTITY OF DISSOLVED ALLOPHANE PRESENT
 IN THE DARK AND REDDISH BROWN SOILS

Sample Number	Amount of Ext. iron in 5 gm soil gms	Fe_2O_3 . <u>85</u> in 5 gm soil	Amount of dissolved allophane in 5 gm soil gms	% dissolved allophane in soils
DZ-1	.125	.1294	.4706	9.41
DZ-5	.150	.1765	.4735	9.47
DZ-9	.345	.4118	.3882	7.76
DZ-13	.455	.5412	.2888	5.78
J-17	.515	.6112	.2588	5.18
J-22	.400	.4706	.2094	4.19
CB-27	.155	.1882	.3818	7.64
CB-32	.150	.1765	.3735	7.47
YG-37	.380	.4471	.3529	7.06
YG-40	.465	.5529	.2971	5.94
A-44	.345	.4235	.3465	6.93
A-47	.155	.1882	.4628	9.23

TABLE V
 QUANTITY OF INTERLAYER ALUMINUM IN DARK AND REDDISH
 BROWN SOILS WITH ORGANIC MATTER PRESENT
 AND WITH ORGANIC MATTER REMOVED

Sample Number	μgm Al/gm	μgm Al/gm soil	% Al in soil	% Al in soil
	+o.m.*	-o.m.	+o.m.	-o.m.
DZ-1	12500	750	1.25	.080
DZ-5	13500	500	1.35	.050
DZ-9	12500	5000	1.25	.500
DZ-13	4000	500	.40	.050
J-17	6500	750	.65	.080
J-22	6500	750	1.40	.080
CB-27	9000	400	.90	.040
CB-32	8000	500	.80	.050
YG-37	7500	25	.80	.003
YG-40	8000	25	.80	.003
A-44	8000	1500	.80	.150
A-47	10000	2000	1.00	.200

*o.m. = organic matter

TABLE VI

CUMULATIVE RELEASE OF POTASSIUM BY CONTINUOUS LEACHING WITH 7 LITERS OF 0.01 N HCL

Sample Number	L.S.*	K μ gm**	L.S.	K μ gm	L.S.	K μ gm	L.S.	K μ gm	L.S.	K μ gm	L.S.	K μ gm	L.S.	K μ gm	L.S.	K μ gm	L.S.	K μ gm
DZ-1-a	260	3300	505	5950	905	7880	1905	8980	2995	9830	3995	12230	4995	15380	5995	17300	6995	18150
DZ-1-b	280	3150	540	5550	840	7480	1840	9410	2840	11000	3840	13190	4840	15380	5840	17920	6840	18170
DZ-5-a	250	3150	500	6440	950	9440	1950	13140	2950	14490	3950	16680	4950	19580	5950	20680	6950	21400
DZ-5-b	250	2900	500	6600	745	9600	1745	11050	2745	13450	3745	15150	4745	18250	5745	19250	6745	20250
DZ-9-a	270	3950	530	10250	980	13950	1980	17350	2980	20130	3980	21710	4980	22560	5980	24840	6980	25440
DZ-9-b	310	3950	584	12150	969	17790	1969	22620	2969	24420	3969	26000	4969	28290	5969	30480	6969	30600
DZ-13-a	250	5180	500	11480	1000	17780	2000	20300	3000	21880	4000	23680	5000	26970	6000	28560	7000	29160
DZ-13-b	250	8000	526	14000	946	19000	1946	23700	2946	26100	3946	28030	4946	30220	5946	31420	6946	32020
J-17-a	216	3700	466	7000	1096	9050	2096	10500	3096	11700	4096	12900	5096	15690	6096	17280	7096	17780
J-17-b	250	3700	510	6480	1010	8660	2010	9260	3010	10110	4010	11310	5010	13610	6010	15070	7010	15670
J-22-a	226	6150	460	11450	960	14250	2060	17330	3060	18910	4060	20610	5060	22430	6060	23780	7060	24380
J-22-b	270	6000	545	11480	1045	14480	2045	15930	3045	17970	4045	19670	5045	23480	6045	24680	7045	25050
CB-27-a	250	1100	404	1820	904	4120	1804	5820	2904	7860	3904	10150	4904	11000	5904	12200	6904	12450
CB-27-b	188	1100	428	2200	888	11380	1888	7780	2888	11070	3888	13470	4888	16000	5888	17700	6888	18550
CB-32-a	360	850	600	1950	930	3400	2030	5690	3090	7970	4090	11190	5090	13720	6090	14920	7090	15770
CB-32-b	250	980	510	2310	750	3410	1750	5330	2750	7250	3750	11480	4750	13060	5750	15250	6750	17050
YG-37-a	370	2530	658	4330	1108	6130	2108	7930	3108	9850	4108	13550	5108	14890	6108	18596	7108	19340
YG-37-b	280	2300	610	4100	1040	5800	2040	7390	3070	9310	4070	13401	5070	14741	6070	16931	7070	19231
YG-40-a	250	1350	546	3150	951	4350	2051	5800	3051	8420	4051	11320	5051	13240	6051	15190	7051	15690
YG-40-b	230	1350	500	3050	950	4030	1950	5330	2950	6680	3950	9700	4950	10900	5950	12700	6950	13700
A-44-a	230	850	500	2050	710	3030	1710	4230	2750	6150	3750	8200	4750	10600	5750	11940	6750	12970
A-44-b	250	980	500	2080	800	3060	1800	4980	2800	6180	3800	8230	4800	10410	5800	11610	6800	12610
A-47-a	250	1200	490	2300	975	3500	1975	5310	2975	6510	3975	8700	4975	10880	5975	12910	6975	13410
A-47-b	306	1200	566	2530	941	3730	1941	5910	2941	7600	3941	9300	4941	10500	5941	11700	6941	12050

*L.S. = Leaching Solution

** μ gm = One Thousandth of a Milligram

TABLE VII
 CUMULATIVE RELEASE OF POTASSIUM BY CONTINUOUS LEACHING WITH 7 LITERS OF 0.01 N HCL
 (AVERAGE VALUE)

Sample Number	L.S.*	K μ gm**	L.S.	K μ gm	L.S.	K μ gm	L.S.	K μ gm	L.S.	K μ gm	L.S.	K μ gm	L.S.	K μ gm	L.S.	K μ gm	L.S.	K μ gm
DZ-1	270	3225	522.5	5750	872.5	7680	1772.5	9195	2872.5	1046.5	3872.5	12710	4927.5	15380	5916.0	17610	6917.5	18160.0
DZ-5	250	3025	500.0	6520	847.5	9520	1847.5	12095	2847.5	1397.5	3847.5	15915	4847.5	18915	5847.5	19965	6847.5	2082.5
DZ-9	290	3950	557.0	11200	974.5	15870	1974.5	19985	2974.5	22275.5	3974.5	23855	4974.5	25420	5974.5	27660	6974.5	28020.0
DZ-13	250	6540	513.0	12740	972.5	18390	1974.0	22000	2973.0	23990.0	3973.0	25855	4973.0	28595	5973.0	29990	6973.0	30590.0
J-17	233	3700	488.0	6740	1053.0	8855	2053.0	9880	3053.0	10905.0	4053.0	12105	5053.0	14650	6053.0	16175	7053.0	16725.0
J-22	245	6075	503.0	11465	1003.0	14365	2053.0	16630	3053.0	18440.0	4053.0	20140	5053.0	22955	6053.0	24230	7053.0	24765.0
CB-27	219	1100	416.0	2010	896.0	4250	1896.0	6800	2896.0	9465.0	3896.0	11810	4896.0	13500	5896.0	14950	6896.0	15500.0
CB-32	305	915	550.0	2130	840.0	3405	1890.0	5510	2920.0	7610.0	3920.0	11335	4920.0	13395	5920.0	15085	6920.0	16410.0
YG-37	325	2415	634.0	4215	1074.0	5965	2074.0	7660	3088.0	9580.0	4089.0	13476	5089.0	14816	6089.0	17760	7089.0	19230.0
YG-40	240	1350	523.0	3100	950.0	4190	2001.0	5565	3001.0	7550.0	4001.0	10510	5001.0	12070	6001.0	13945	7001.0	14695.0
A-44	240	910	500.0	2060	750.0	3045	1755.0	4605	2775.0	6165.0	3775.0	8215	4755.0	10505	5775.0	11775	6775.0	12790.0
A-47	273	1200	528.0	2410	958.0	3615	1958.0	5610	2958.0	7055.0	3958.0	9000	4958.0	10690	5958.0	12305	6958.0	12730.0

*L.S. = Leaching Solution
 ** μ gm = One Thousandth of a Milligram

in respect to magnitude of the potassium release as did the Jimma soils (Figure 4). The College Blackland soils (Figure 3) and the Asmara soils (Figure 6) were not variable in this regard, although some variation was observed for the Yerer Gota Fruit Farm soils (Figure 5). All the blackland soils were similar in that easily releaseable potassium was obtained within the one to two liters leaching. For the reddish brown soils the easily replaceable potassium was obtained within the one to two and one-half liter leaching range.

In general, the cumulative potassium release studies for both the blackland and reddish brown soils indicated that there was continuous release of potassium with continued leaching up to approximately the seventh liter of 0.01 N HCl. In some cases change in slope is noted on these curves which is probably due to experimental error. The Ca, Mg, and Na data are appended.

Garman's work included using continuous leaching with 0.01 N HCl, rapid microchemical, boiling nitric acid extraction, and exchangeable methods used were for the removal of potassium, and the results obtained with each method were compared with the quantity of potassium removed by an eleven month cropping removal. It was shown that the form, rate, and quantity removed by each method was variable with variation in soils. Reitmeir (46) and Peech (42) discussed the measurement of potassium by various techniques. Solutions of relatively low pH are recommended according to Garman (18) for extracting potassium in order to obtain the release of the more strongly adsorbed potassium. The advantage with this method lies in that it is possible to characterize the rate of potassium release of different soils of about the same level of exchangeable potassium. Also, solutions such as a 0.01 N HCl

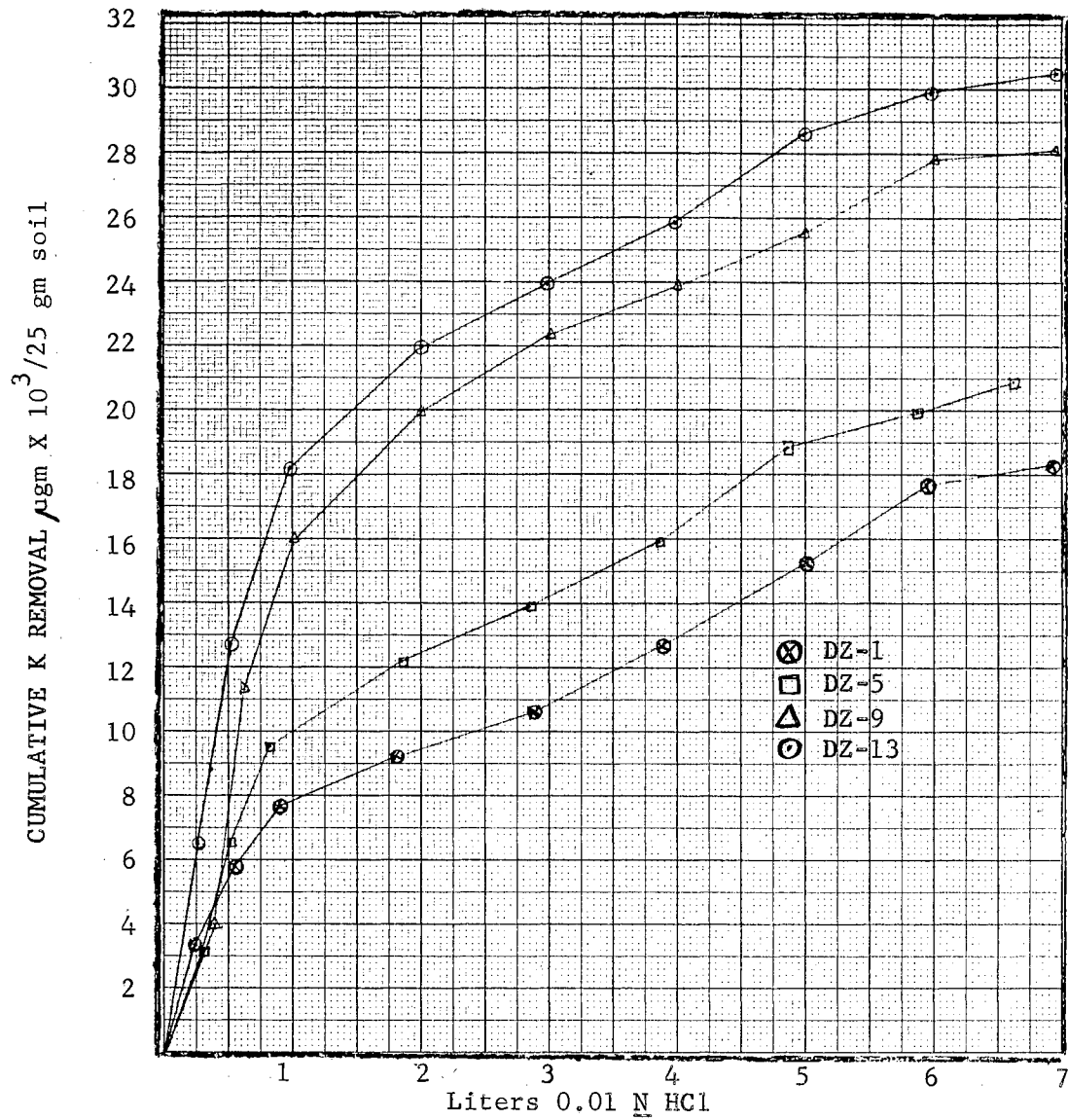


Figure 2. Accumulative potassium release curve for Debre-Zeit blackland soils resulting from continuous leaching with 0.01 N HCl.

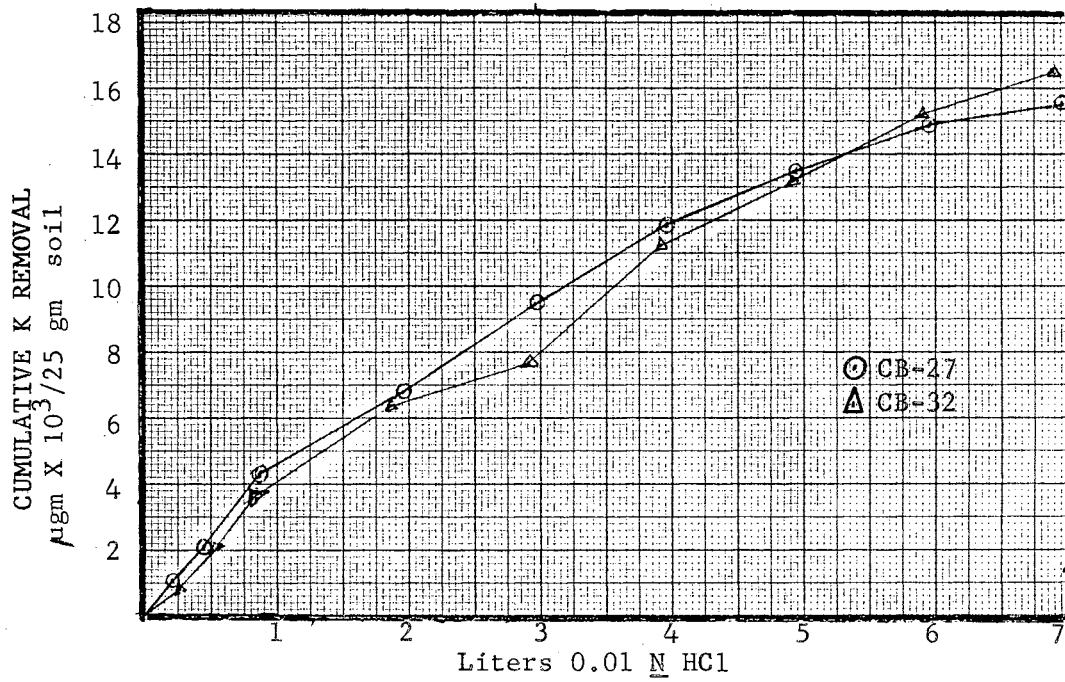


Figure 3. Accumulative potassium release curve for College Blackland (CB-27,32) soils resulting from continuous leaching with 0.01 N HCl.

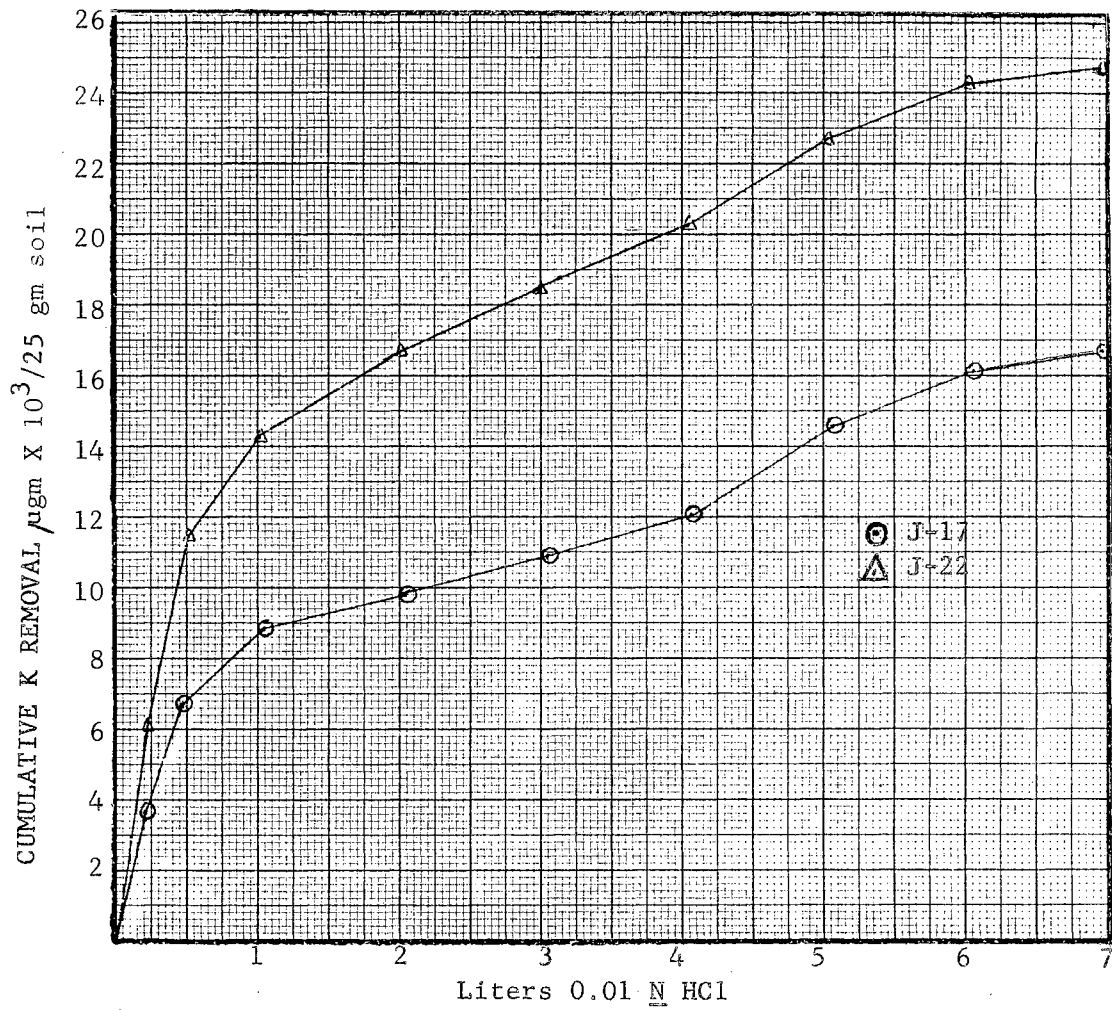


Figure 4. Accumulative potassium release curve for Jimma (J-17, 22) reddish brown soils resulting from continuous leaching with 0.01 N HCl.

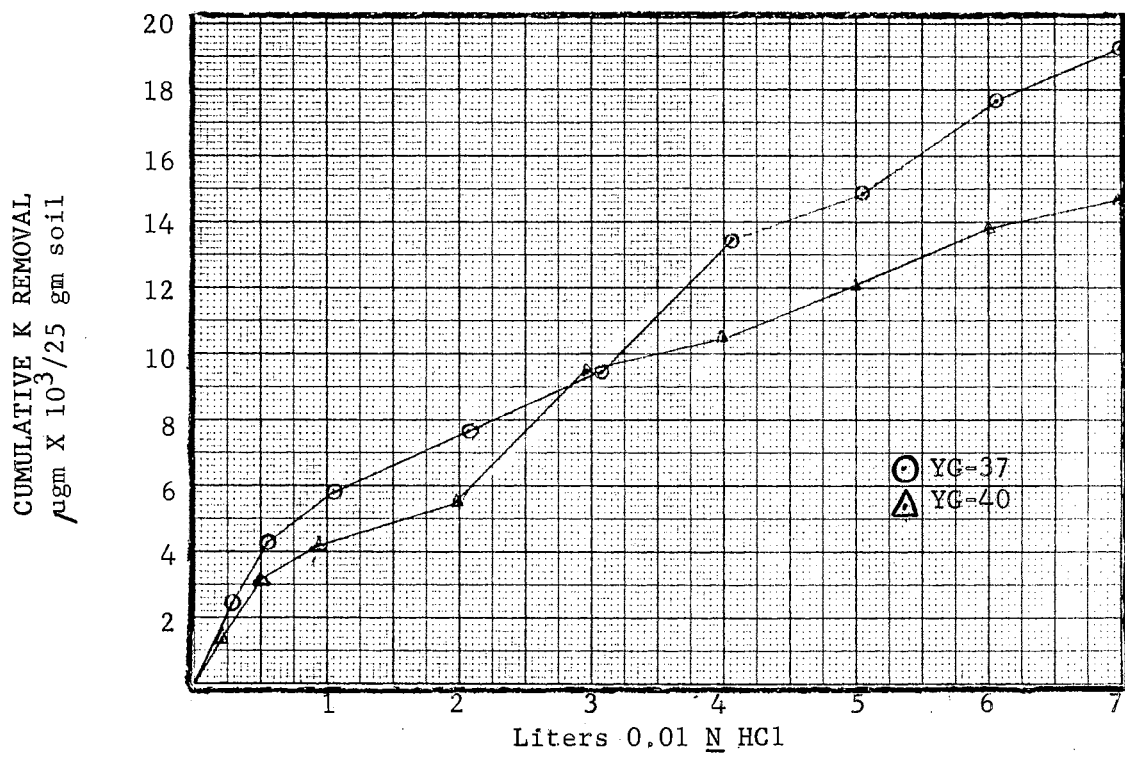


Figure 5. Accumulative potassium release curve for Yerer Gota (YG-37, 40) soils resulting from continuous leaching with 0.01 N HCl.

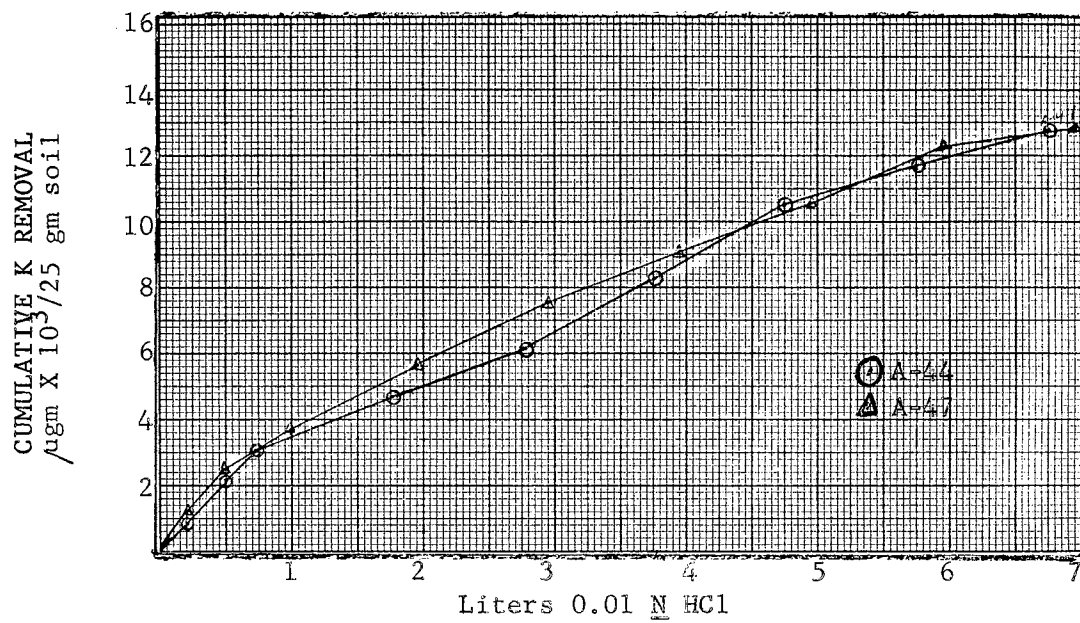


Figure 6. Accumulative potassium release curve for Asmara (A-44,47) blackland soils resulting from continuous leaching with 0.01 N HCl.

of pH 2.0 are preferable because the Hydrogen ion is a most effective agent for potassium replacement. The concentration is adequate to remove both adsorbed and structural forms at a rate suitable for rapid evaluation in the laboratory, and the dilute concentration enables the removal without altering or destroying the crystalline structure of the silicate minerals. Of the various methods employed in connection with Garman's work (18), the continuous leaching with 0.01 N HCl was reported to have consistently given the highest correlation coefficients for surface and subsoil samples and the lowest errors of estimate. Although the concentration of potassium in the leaching solution appeared to be very low, being less than 0.1 ppm. in many soils even with a 0.01 N HCl solution after leaching with 2 or 3 liters of the solution, the method gave the smallest Y-intercept value and a slope approaching unity; this signified that the quantities of potassium removed by it were closer in equivalence to removal by crops than was the case with any of the other methods. It is to be noted that Garman suggested that emphasis should be given not only to the close correlation but more so to this equivalency of removal.

The advantage attached to the cumulative release by continuous leaching is that it is possible to align the quantity of leachate to the length of cropping with the view that one can determine equivalent removal under different growth periods. The higher correlation found by Garman for the longer leaching period was attributed to the closer relationships existing between continuous plant uptake of potassium and the rate of release from structural potassium forms commonly occurring during the last 5 to 10 liters of leaching.

Schmitz and Pratt (51) reported correlation coefficients for the

soils described by Garman to be 0.899 for "crops" vs. "exchangeable K" uptake, 0.902 for "crops" vs. "total K in HNO_3 extraction" and 0.959 for "crops" vs. "exchangeable before cropping plus HNO_3 extraction" calculated by multiple correlation analysis. It was found, however, that although these correlations were highly significant, the quantities of potassium removed by the exchangeable method were significantly less than those removed by crops; the removal by HNO_3 resulted in quantities several times that removed by crops. Related findings indicated that it could be inferred that rating values such as low, medium, and high would not be correlated in the same range for surface and subsoils. Garman found in this connection that the amount of K removed by the soil quick test was approximately 80% of the exchangeable K for surface soils but less than this for subsoils.

By empirical estimate, the soils studied are found to be highly granular, and although aluminum interlayering contributes to this slightly, much of the granularity is apparently attributable to the organic matter. The extent of aluminum interlayering in the clay fraction is low, ranging from a minimum of .40 percent to a maximum of 1.40 percent for all the soils before organic matter was removed; and the value ranged from .003 percent for the College Blackland soils to a high of .200 percent for the Asmara soils, after the organic matter was removed.

PART V. SUMMARY AND CONCLUSIONS

In general, the cation exchange capacity values were higher for the vertisols of the Debre-Zeit, Yerer Gota, College Blackland, and Asmara areas than was the case for the Oxisols of the Jimma area. No significant difference in these values was obtained by using the two different methods, and the cation exchange delta values as well as the percent allophane in the soils were low. This indicates that these Ethiopian soils are not allophanic. According to the findings in this study, the vertisols were montmorillonitic, and the Jimma area oxisols, kaolinitic.

A small amount of interlayer aluminum was found in all cases, but no significant correlation was observed between this interlayer aluminum and the delta values. By empirical estimate, it was also shown that the soils are granular.

No correlation was found between the potassium and interlayer aluminum; however, the potassium supplying power of the soil is considered to be good.

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APPENDICES

APPENDIX A

Symbols used in this study and their meanings:

DZ = Debre-Zeit

CB = College Blackland

J = Jimma

YG = Yerer Gota

A = Asmara

TABLE VIII

CUMULATIVE RELEASE OF SODIUM BY CONTINUOUS LEACHING WITH 7 LITERS OF 0.01 N HCL

Sample Number	L.S.*	Na μ gm**	L.S.	Na μ gm	L.S.	Na μ gm	L.S.	Na μ gm	L.S.	Na μ gm	L.S.	Na μ gm	L.S.	Na μ gm	L.S.	Na μ gm	L.S.	Na μ gm
DZ-1-a	260	650	505	750	905	1100	1905	1200	2995	1450	3995	1850	4995	2150	5995	2400	6995	2400
DZ-1-b	280	500	540	600	840	950	1840	1150	2840	1500	3840	2000	4840	2350	5840	2650	6840	2650
DZ-5-a	250	400	500	580	950	830	1950	1280	2950	1380	3950	1630	4950	1980	5950	2080	5960	2080
DZ-5-b	250	500	500	600	745	1100	1745	1300	2745	1550	3745	1550	4745	1800	5745	2050	6745	2050
DZ-9-a	270	500	530	1150	980	1400	1980	1900	2980	2600	3980	3800	4980	4150	5980	4300	6980	4700
DZ-9-b	310	650	584	1150	969	1700	1969	2400	2969	2900	3969	4300	4969	4600	5969	4950	6969	5250
DZ-13-a	250	650	500	1150	1000	1650	2000	2150	3000	2650	4000	4050	5000	5550	6000	6450	7000	6550
DZ-13-b	250	900	526	1250	946	1500	1946	1850	2946	2000	3946	3400	4946	3550	5946	4550	6946	4900
J-17-a	216	800	466	900	1096	1150	2096	1250	3096	1450	4096	1600	5096	2300	6096	2400	7096	2500
J-17-b	250	500	510	600	1010	800	2010	900	3010	1400	4010	1550	5010	1650	6010	1750	7010	2000
J-22-a	220	400	460	500	960	1000	2060	1100	3060	1250	4060	1400	5060	1550	6060	1650	7060	2450
J-22-b	270	350	545	450	1045	550	2045	650	3045	800	4045	950	5045	1300	6045	1650	7045	1750
CB-27-a	250	550	404	750	904	2030	1904	2580	2904	2730	3904	3030	4904	3130	5904	3230	6904	3230
CB-27-b	188	550	428	650	888	1200	1888	1300	2888	1400	3888	1650	4888	1900	5888	2300	6888	2450
CB-32-a	360	750	600	1000	930	1100	2030	1200	3090	1300	4090	1450	5090	1550	6090	2350	7090	2450
CB-32-b	250	1100	510	1800	750	1900	1750	2000	2750	2500	3750	2700	4750	3000	5750	3150	6750	3150
YG-37-a	370	1350	658	1450	1108	2550	2108	2900	3108	3050	4108	3400	5108	3500	6108	3750	7108	3900
YG-37-b	280	1290	610	1390	1040	1590	2040	1960	3070	1840	4070	2190	5070	2340	6070	2690	7070	2790
YG-40-a	250	1290	546	1390	951	1490	2051	1590	3051	1690	4051	2040	5051	2740	6051	2840	7051	2940
YG-40-b	230	1350	500	1700	950	2250	1950	2500	2950	2600	3950	3500	4950	3800	5950	3900	6950	3900
A-44-a	230	2650	500	3150	710	4050	1710	4700	2750	4950	3750	5850	4750	6550	5750	6650	6750	7000
A-44-b	250	2650	500	3150	800	3550	1800	4250	2800	4500	3800	5400	4800	5700	5800	5800	6800	5800
A-47-a	250	2000	490	3000	975	3650	1975	4450	2975	4700	3975	6200	4975	6300	5975	7000	6975	7400
A-47-b	306	2000	566	3000	941	3500	1941	4300	2941	4800	3941	6300	4941	7200	5941	7900	6941	8300

*L.S. = Leaching Solution

** μ gm = One Thousandth of a Milligram

TABLE IX
 CUMULATIVE RELEASE OF CALCIUM BY CONTINUOUS LEACHING WITH 7 LITERS OF 0.01 N HCL

Sample Number	L.S.*	Ca μ gm**	L.S.	Ca μ gm	L.S.	Ca μ gm	L.S.	Ca μ gm	L.S.	Ca μ gm	L.S.	Ca μ gm	L.S.	Ca μ gm	L.S.	Ca μ gm	L.S.	Ca μ gm
DZ-1-a	260	137.5	505	382.0	905	640.0	1905	780.0	2995	880.0	3995	1053.0	4995	1413.0	5995	1468.0	6995	1528.0
DZ-1-b	280	172.8	540	380.8	840	580.0	1840	780.0	2840	959.0	3840	1139.0	4840	1469.0	5840	1521.0	6840	1572.0
DZ-5-a	250	162.0	500	503.0	950	803.0	1950	978.0	2950	1053.0	3950	1132.0	4950	1240.0	5950	1300.0	6950	1325.0
DZ-5-b	250	139.5	500	451.5	745	785.5	1745	918.5	2745	1020.5	3745	1141.5	4745	1243.5	5745	1303.0	6745	1328.0
DZ-9-a	270	125.0	530	268.5	980	568.5	1980	658.5	2980	802.5	3980	828.5	4980	945.5	5980	1083.5	6980	1100.5
DZ-9-b	310	65.0	584	335.0	969	651.0	1969	830.0	2969	1007.0	3969	2263.0	4969	2368.0	5960	2506.0	6960	2523.0
DZ-13-a	250	92.0	500	392.0	1000	530.0	2000	668.0	3000	757.0	4000	1941.0	5000	2016.0	6000	2154.0	7000	2161.0
DZ-13-b	250	162.0	526	478.0	946	946.0	1946	1089.0	2946	1353.0	3946	2473.0	4946	2526.0	5946	2653.0	6946	2662.0
J-17-a	216	116.5	466	312.0	1096	342.0	2096	444.0	3096	528.0	4096	553.0	5096	671.0	6096	713.0	7096	719.0
J-17-b	250	118.5	510	318.5	1010	506.5	2010	606.5	3010	636.5	4010	661.5	5010	795.5	6010	872.5	7010	899.5
J-22-a	220	79.0	460	235.0	960	255.0	2060	374.0	3060	499.0	4060	560.0	5060	694.0	6060	740.0	7060	757.0
J-22-b	270	77.0	545	226.5	1045	401.5	2045	528.5	3045	582.5	4045	136.8	5045	1528.5	6045	1574.5	7045	1580.5
CB-27-a	250	114.5	404	301.5	904	617.5	1904	1657.5	2904	2713.5	3904	2786.5	4904	3090.5	5904	3157.5	6904	3170.5
CB-27-b	188	170.5	428	486.5	888	1266.5	1888	2434.5	2888	2704.5	3888	2783.5	4888	3043.5	5888	3098.5	6888	3107.5
CB-32-a	360	95.8	600	287.3	930	687.3	2030	1069.3	3090	1443.3	4090	2051.3	5090	2263.3	6090	2318.3	7090	2327.3
CB-32-b	250	126.5	510	666.5	750	978.5	1750	1466.5	2750	2266.5	3750	2446.5	4750	2642.5	5750	2726.5	6750	2749.5
YG-37-a	370	270.0	658	810.0	1108	978.0	2108	2426.0	3108	3490.0	4108	3890.0	5108	4079.0	6108	4206.0	7108	4366.0
YG-37-b	280	183.0	610	707.0	1040	1423.0	2040	2399.0	3070	3655.0	4070	4055.0	5070	4277.0	6070	4379.0	7070	4579.0
YG-40-a	250	166.0	546	774.0	951	974.0	2051	1774.0	3051	3070.0	4051	4190.0	5051	4401.0	6051	4486.0	7051	4656.0
YG-40-b	230	141.5	500	544.5	950	741.5	1950	979.5	2950	1379.5	3950	1400.5	4960	1600.5	5950	1694.5	6950	1849.5
A-44-a	230	131.0	500	418.0	710	456.0	1710	818.0	2750	1218.0	3750	1992.0	4750	2740.0	5750	2867.0	6750	3027.0
A-44-b	250	64.5	500	322.5	800	686.5	1800	1086.5	2800	1486.5	3800	2286.5	4800	3086.5	5800	3224.5	6800	3404.5
A-47-a	250	96.0	490	349.0	975	719.0	1975	912.0	2975	1312.0	3975	1828.0	4975	1982.0	5975	2111.0	6975	2136.0
A-47-b	306	100.0	566	358.0	941	720.0	1941	911.0	2941	1311.0	3941	1827.0	4941	1962.0	5941	2089.0	6941	2134.0

*L.S. = Leaching Solution
 ** μ gm = One Thousandth of a Milligram

TABLE X
 CUMULATIVE RELEASE OF MAGNESIUM BY CONTINUOUS LEACHING WITH 7 LITERS OF 0.01 N HCL

Sample Number	L.S.*	Mg /ugm**	L.S.	Mg /ugm	L.S.	Mg /ugm	L.S.	Mg /ugm	L.S.	Mg /ugm	L.S.	Mg /ugm	L.S.	Mg /ugm	L.S.	Mg /ugm	L.S.	Mg /ugm
DZ-1-a	260	77	505	277	905	402	1905	445	2995	478	3995	550	4995	560	5995	560	6995	580
DZ-1-b	280	89	540	244	840	384	1840	473	2840	489	3840	559	4840	579	5840	579	6840	589
DZ-5-a	250	48	500	138	950	203	1950	273	2950	453	3950	523	4950	563	5950	563	6950	573
DZ-5-b	250	17	500	97	745	197	1745	403	2745	589	3745	614	4745	684	5745	684	6745	699
DZ-9-a	270	5	530	65	980	154	1980	414	2980	554	3980	644	4980	734	5980	734	6980	859
DZ-9-b	310	7	584	82	969	132	1969	378	2969	470	3969	700	4969	845	5969	845	6969	370
DZ-13-a	250	50	500	105	1000	185	2000	431	3000	546	4000	776	5000	941	6000	941	7000	1051
DZ-13-b	250	50	526	105	946	205	1946	305	2946	410	3946	640	4946	800	5946	800	6946	985
J-17-a	216	51	466	136	1096	181	2096	226	3096	246	4096	256	5096	341	6096	341	7096	356
J-17-b	250	53	510	151	1010	226	2010	261	3010	316	4010	326	5010	386	6010	386	7010	401
J-22-a	220	49	460	124	960	149	2060	196	3060	221	4060	231	5060	416	6060	416	7060	506
J-22-b	270	50	545	135	1045	210	2045	245	3045	270	4045	280	5045	370	6045	370	7045	390
CB-27-a	250	35	404	60	904	165	1904	343	2904	543	3904	708	4904	768	5904	1348	6904	1423
CB-27-b	188	35	428	80	888	202	1888	402	2888	467	3888	632	4888	712	5888	802	6888	812
CB-32-a	360	30	600	98	930	203	2030	320	3090	420	4090	615	5090	690	6090	810	7090	820
CB-32-b	250	37	510	117	750	192	1750	322	2750	422	3750	562	4750	637	5750	967	6750	997
YG-37-a	370	167	658	313	1108	388	2108	558	3108	133	4108	748	5108	808	6108	808	7108	843
YG-37-b	280	95	610	241	1040	343	2040	443	3070	543	4070	656	5070	716	6070	751	7070	826
YG-40-a	250	65	546	180	951	255	2051	425	3051	557	4051	677	5051	737	6051	1087	7051	1162
YG-40-b	230	70	500	183	950	258	1950	403	2950	478	3950	596	4950	686	5950	1076	6950	1168
A-44-a	230	71	500	271	710	386	1710	686	2750	912	3750	1057	4750	1257	5750	1372	6750	1517
A-44-b	250	68	500	198	800	308	1800	628	2800	852	3800	1027	4800	1227	5800	1237	6800	1397
A-47-a	250	70	490	195	975	395	1975	715	2975	915	3975	1080	4975	1230	5975	1239	6975	1372
A-47-b	306	69	566	192	941	390	1941	710	2941	910	3941	1055	4941	1235	5941	1400	6941	1545

*L.S. = Leaching Solution
 **ugm = One Thousandth of a Milligram

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