POTASSIUM RELEASE CHARACTERISTICS OF SELECTED PERUVIAN SOILS

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ABSTRACT

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By

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Results from soil fertility experiments in Peru have indicated that the ability to predict a response to added potassium (K) fertilizer is not adequate. To evaluate the K status of some Peruvian soils, samples from 16 soils were shipped to Michigan State University where they were intensively cropped using the Stanford-DeMent technique, and K release was studied using sodium tetraphenylboron (NaTPB) for varying time periods. The amounts of K removed and rates of K release were then related to the clay mineral composition of the soil, and the soil solution, exchangeable, and total K contents of the soils.

When 1 g soil samples were equilibrated with solutions containing NaTPB for 0.25, 1, 10, 100, 1000 and 2000 hours, a linear relationship was found between K removed by NaTPB and the logarithm of time from 10 to 1000 hr. Rates of K release varied from -0.03 to 7.43 me K/100 g

soil/wk. Large differences in the total amount of K removed after 2000 hr (1.9 to 66.9 me K/100 g soil) were well related to the presence and apparent degree of crystallinity of the illite in the clay fraction. Variations in rate of K release and sources of plant-available K appeared to explain why a poorer relationship between the K extracted with NaTPB for 15 min and K uptake by cropping ($r = 0.643$) was obtained than has previously been reported.

Amounts of plant-available K and rates of K release as determined from cumulative K uptake from five successive, two-week oat crops varied from 0.35 to 3.24 me K/100 g soil and 0.016 to 0.215 me K/100 g soil/wk, respectively. Total K uptake was not well correlated with K extracted with ammonium acetate ($r = 0.388$); the correlation was improved by considering K uptake from only the first of the five crops ($r = 0.693$) and was much higher when only K uptake from those soils with low K supplying capabilities were used in computing the correlation coefficient ($r = 0.979$). Total K in the soils was better related with K uptake by plants as cropping progressed indicating that higher amounts of K were being removed from nonexchangeable forms. Potassium uptake from those soils which released high amounts of K by cropping and with NaTPB was correlated

somewhat higher with the percent K in the sand than with the percent K in the silt, which suggests that these soils are relatively unweathered. The concentration of K in the soil solution was not correlated with K uptake by plants for any of the croppings.

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A THESIS

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TO JEAN

This thesis is affectionately dedicated

to my wife. . .

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INTRODUCTION

The diversity in climate, agricultural crops and soils in Peru and the scarcity of arable land present a challenge for those workers whose goal is increasing food production. Only 8.6% of the land area of Peru is suitable for intensive agriculture, 53.5% of the land should be used for only permanent types of agriculture and the remaining 37.9% is unusable for agricultural purposes (Zamora, 1969). Land which can be used for agricultural purposes is found in ecological zones which include tropical, desert and sub-alpine as well as the transitional areas between these different zones (Tosi, 1960).

If food production in Peru is to keep pace with the population growth, increased production must be obtained on those soils now under cultivation, and new lands which are capable of producing food must be brought under cultivation. The use of chemical fertilizers is one of the necessary components in an increased food production program; however, fertilizers in a developing country are costly and thus must be used as efficiently as possible.

Field experimental work in recent years has shown that the ability to predict a response to potassium (K) fertilizers has not been satisfactory and a recommendation as recent as 1970 was that studies be made which would lead to a better evaluation of the availability of nonexchangeable K to crops in Latin America (Fitts, 1970).

A study was initiated in Peru and completed at Michigan State University (MSU) to evaluate the K-supplying ability of selected soils from the mountains (sierra), jungle and coast of Peru. Two Michigan soils were included in the study to make comparisons in amounts of K removed and rates of K release with the Peruvian soils.

LITERATURE REVIEW

The Soils of Peru

The soils of Peru are probably as variable as in any country in the world due to the extreme variability in the five soil-forming factors: climate, vegetation, relief, parent material and time. The few soil maps which are available are general in their soil descriptions (Zamora, 1969). When describing these soils the country is usually divided into three geographical regions: the arid western coast, the central Andean mountains and the eastern tropical lowlands (Zavaleta and Arca, 1963; Drosdoff et al., 1960).

Arid western coast

The soils of this region are found in a narrow band from 50 to 100 kilometers wide along the Pacific Coast. They have received essentially no rainfall due to the presence of the cool Humboldt current and the Andean mountains and thus are relatively unweathered. The four main soil groups recognized by Drosdoff et al. (1960) are alluvial, desert lithosol, desert regosol and red and gray desert.

Central Andean highlands (sierra)

Jan Beek and Bramao (1968) describe this region as follows:

> The Andean mountain ranges are composed of a western range of marine Mesozoic and more recent volcanic rocks, with an elongated batholitic core, and an eastern chain of folded sedimentary, often Palaeozoic, rocks with scattered older granite and schist outcrops.

The high variability of the soils is due principally to intensive erosion, sedimentation and accumulation of colluvial material. Zavaleta and Arca (1963) recognized alluvial, lithosol, brown, Andean meadow, chernozem and rendzina, humic gley, and organic soils as the major groups of this area. This was similar to the groupings described by Drosdoff et al. (1960) who listed lithosols of the arid western slopes, the Andean valley association, puna association, titicaca association, lithosols and hydromorphs of the very high mountains and soils of the frigid region as the major groups.

There is limited information available regarding the clay mineralogy of these soils. Miller and Coleman (1952) identified montmorillonite and illite in the dark-colored Paramo (probably puna association) soils. There was also some evidence for the presence of non-crystalline

minerals. Amorphous materials could be expected to be present in the soils of the north and south of Peru if they are volcanic in origin (Zavaleta, 1969). The soils in the moist regions of the sierra also contained kaolinite as well as expanding lattice and illite clay minerals.

Eastern tropical lowlands

This area, dominated by the Amazon Basin, consists mainly of Tertiary and Pleistocene unconsolidated sediments that contain mainly kaolinitic clays and quartz sands (Jan Beek, and Bramao, 1968). The acid tropical soils of the eastern forests as outlined by Estrada (1971) include spodosols, ultisols and oxisols. The clay mineralogy of these soils suggest one group which has a predominance of 1:1 type lattice clay minerals and another group that contains equal or greater amounts of 2:1 type clay minerals. Similar results were obtained by Sanchez and Buol (1971) who reported the presence of Paleudalts which were predominantly kaolinitic with smaller amounts of montmorillonite in some cases and poorly drained Paleudalfs, Tropaquepts and Tropaqualfs in which the clays were predominantly montmorillonitic or of mixed mineralogy.

Forms of Soil Potassium

Total K levels in soils are among the highest of any of the soil-derived plant nutrients. Bowen (1966) reported an average total K value for soils of 1.40% with a range from 0.03 to 3.00%. Other values given for the United States range from less than 0.3% in the southeast and southern coastal plain to 2.5% in the midwest and west (Tisdale and Nelson, 1966). Failyer, et al. (1908) reported a tendency for the K concentration in soil fractions to increase as the particle size decreased. However, a wide variation would be expected due to different degrees of weathering and kinds of parent material. Native soil K sources are the feldspars, micas and micaceous clay minerals. Jackson (1948) classifies the feldspars as framework silicates and the micas and micaceous clay minerals as layer silicates.

Framework silicates

Structure: The framework silicates are characterized by a lattice formed by a sharing of four oxygens (Jackson, 1948). When aluminum and potassium are partially substituted for the silica in the oxygen tetrahedra, the formula for the potassium feldspars, orthoclase and

microcline, is obtained ($K(AlSi)_4O_8$). In general, the feldspars are found in the sand and silt fraction and release only small amounts of K to a plant-available form during any one cropping season.

Methods of potassium release: By evaluating the amounts of different feldspars present in a podzol profile from the Netherlands, Van der Marel (1949) estimated that about 8-15 kg K_2O/Ha (30cm) became available each year from feldspars. Biological agents appear to be one of the more effective mechanisms of feldspar weathering. The decomposition of feldspars with the subsequent formation of SiO_2 and Al_2O_3 was demonstrated by Novorossova et al. (1947) by placing feldspars in contact with a mixed microflora in a medium containing glucose and organic N. Bassalick (1912), working with selective bacterial cultures, observed appreciable decomposition of feldspar where the micro-organisms formed a continuous film on the mineral particles. The stability of this weathering film and the particle size are factors which Arnold (1960) gives as controlling K release from feldspars.

Layer silicates

Structures: The major native sources of K for plant growth are the layer silicates of which the micas and illites predominate in importance. The two basic structures in the layer silicates are the silica tetrahedron and the aluminum octahedron. A unit cell is comprised of two tetrahedral layers with their apices pointed in towards an octahedral layer between them. If there are two aluminum ions in the octahedral layer the mineral is considered to be dioctahedral, and if there are three divalent cations such as iron and magnesium instead of two aluminum ions in the octahedral layer, the mineral is said to be trioctahedral. General forumulas for muscovite (dioctahedral) and biotite (trioctahedral) micas are $(OH)_4K_2(Si_6 \cdot Al_2)Al_4O_{20}$ and $(OH)_4K_2(Si_6 \cdot Al_2)(Mg \cdot Fe)_6O_{20}$, respectively (Grim, 1968).

The term illite, used for the major K bearing mineral in the clay fraction, has not always been well defined. Gandette et al. (1964) analyzed a series of clay samples and concluded that illites have less K than the well-crystallized micas and are not necessarily mixed-layer materials. Less aluminum substitution for silica in the tetrahedral layers resulting in a lower net charge and

partial replacement of K from the interlayer spaces by other cations are possible variations of the illites from the true micas given by Grim (1968). Thus illite is probably secondary in origin and is found mainly in the clay fraction, while the more crystalline micas which may be found either primary or secondary in origin are usually found in the silt and sand fractions (Black, 1968).

Potassium release mechanisms: For the feldspars, complete destruction of the structure is necessary for K to be released. However, the layered structure of micas and illite permits K to diffuse out with a minimal disruption of the mineral. Theories describing K weathering have been proposed by Jackson et al. (1952), Reed and Scott (1962), Mortland (1958, 1961), Newman and Brown (1966) and Tucker (1964) and excellent reviews are given by Reitemeier (1951) and Rich (1968).

In the weathering sequence of the layer silicates as proposed by Jackson et al. (1952), depotassication, hydroxylation, dealumination and disilication are essential chemical reactions. The removal of K, or depotassication, is the necessary first step and is based on the preferential weathering plane theory, i.e. micas weather along a given

potassium plane at a rate order of magnitude faster (once the weathering is initiated) than the rate of initiation of weathering of such a plane, and alternate mica interplanes weather more easily than the remaining interplanes (particularly dioctrahedral micas). The driving force for the above process is the entrance of water and hydrated cations between the layers.

Reed and Scott (1962) essentially expanded this theory when they proposed a circular disc as a model for a mica particle and determined rates of release of K by precipitating it in solution with sodium tetraphenylboron (NaTPB). In this system, in contrast to Jackson's theory, the initial rate of K release was higher than that after more K had been removed. They concluded that diffusion within the particle was the rate-limiting step in K release (Scott and Reed, 1962).

When samples of biotite were leached with 0.1 N NaCl, Mortland (1958) found that the rate of K release was independent of the amount of K in the mineral until 75% of the K had been removed after which time there was a logarithmic relation between the rate of K release and time. It was later concluded that diffusion of K and Na ions through the film surrounding the particle was the

rate-limiting process (Mortland and Ellis, 1959). Although there appears to be a discrepancy in the above two theories, both appear to be valid conclusions in view of the experimental conditions which existed (TPB precipitating K in solution in one case and K being removed by leaching in the other case).

Factors affecting weathering rates: The weathering of micas and illites is more easily understood when some of the factors which affect it are considered. Type of mica, particle size and pH of the environment are among the major factors which influence K weathering rates.

There is a general consensus among researchers that the K in dioctahedral micas and illites is more resistant to release than K in trioctahedral micas and illites. Weed et al. (1969) removed 63% of the K from biotite and 20% of the K from muscovite by placing the minerals in contact with fungi in a buffered nutrient solution. The fungi provided a sink for K and kept the soil solution K at a low level. Scott and Smith (1966) used NaTPB as a precipitating agent for K to keep the soil solution K level low. They removed essentially all of the K from vermiculite, biotite and muscovite, but only 66% of the K from illite.

They had postulated earlier that interlayer material made the remaining K inaccessible to exchange (Smith and Scott, 1966). Differential K release due to type of mica has been explained by differences in the orientations of the O-H bonds (Quirk and Chute, 1968; Leonard and Weed, 1970), length of the K-O bond (Leonard and Weed, 1970; 1970) and charge densities as indicated by calculated Si/Al ratios (Ross and Kodama, 1970).

The release of both fixed K and native K to plants was investigated by Mortland et al. (1957). They noted a comparatively rapid release of K fixed by montmorillonite and vermiculite and native biotite. The release of K from illite and muscovite was more difficult. Further investigation by Ellis and Mortland (1959) showed that the release of K from native biotite was at a constant rate while approximately 50% of the K was removed whereas the rate of release from fixed forms of K decreased with time.

Amount and rate of release of K from micas as affected by particle size appear to be related to the amount of stress applied to the particle. Initially the smaller biotite particles released more K when they were leached with 0.1 N NaCl (Mortland and Lawton, 1961). However, after 50% of the total K had been removed, the larger

particles had lost as much K as the finer particles (1-250 μ). Reichenbach and Rich (1969), using 0.1 N $BaCl_2$ at 120 C in a repeated batch technique, found that 92% of the K in larger muscovite particles (5-20 μ) was released while in the smaller particles (0.08-27 μ) only 57% was released. Similar results were obtained by Scott (1968) by equilibrating different particle sizes of muscovite with NaTPB; however, the smaller particles (0.2-0.7 μ) initially released more K than the larger particles (50-60 μ). He proposed that although both edge and layer weathering were taking place the predominant mechanism changed from edge to layer weathering with a decrease in particle size. Thus if there is an initial high loss of K due to layer weathering in the small particles, the remaining K in the next interlayer will be more tightly bound as was proposed by Bassett (1959). This agrees with results found by Doll et al. (1965) when soil clays were cropped in the greenhouse.

The effect of pH on the release of K from micas and illites is not always clear. When NaTPB was used as the potassium sink in a buffered solution, Scott and Smith (1966) found that muscovite (50 μ), biotite (50 μ) and illite (2 μ) all released more K at solution pH values of

4.6 than at 7.2 or 9.2. The differences were greater for biotite than for muscovite or illite. These same workers have also reported that solution pH had essentially no effect on the amount of K removed from a grundite illite (Smith and Scott, 1966). Huang et al. (1968) found that muscovite and biotite released more K where they were equilibrated in dilute HCl solutions than in distilled water. A much wider range in pH values was used by Tucker (1964) with soil illites. The K release decreased as pH increased to pH 11 and then began to increase again. He concluded that below pH 11 K release is due to instability of the clay mineral structure towards hydrogen ions or to displacement of K by other cations acting together with hydrogen ions; above pH 11 the release is due to breakdown of the clay mineral. Based on studies on the action of dilute HCl and NaCl solutions on a lepidomelane-biotite flake, Wells and Norrish (1968) concluded that the hydrogen ion can replace interlayer K by the same general processes as do other cations and in addition it can at high concentrations dissolve the mica.

Release of Soil Potassium to Plants

Equilibrium reactions which determine the K found in the soil solution, on exchange sites, and in the clay lattice will govern the ability of a soil to release K to plants. Thomas and Hipp (1968) stated that the equilibrium between the K in the soil solution and exchangeable K is of major importance for K availability to plants for time periods shorter than a several years while the nonexchangeable-exchangeable K equilibrium is an important consideration for sustained plant growth for longer periods of time.

Much of the current information regarding the weathering of K from pure minerals is based on establishing an efficient sink for K. The low K contents in the soil solution provide an excellent concentration gradient causing increased diffusion of K from the mineral. Scott and Smith (1966) using NaTPB increased the amount of K removed from biotite from 30% to 100% by decreasing the K in solution from 10 to 7 ppm. They also found that soil solution K levels as low as 0.1 ppm restricted the removal of K from muscovite to 17% of the total K. The level of K in the actual soil solution is usually much higher than this. Asher and Ozanne (1967) reported that for 14 plant species, a K

concentration between 24 and 95 uM in solution was necessary for normal plant growth. Barber (1962) reported soil solution K values from the literature which ranged from 3 to 156 ppm. For soils with high concentrations of K in the soil solution, mass flow and not diffusion may be the predominant mechanism supplying K for plant growth. It would seem, therefore, that solution K measurements would be a valid criteria if they were considered with exchangeable K determinations. Hipp and Thomas (1967) found this to be true. They obtained a good correlation ($r = 0.890$) between the percent K in sorghum leaves at full bloom and solution K + log (1 + exchangeable K).

The amount of K which is released from lattice forms to a plant-available form will be determined by the combination of clay minerals present in the soil, their size distribution and exchangeable K levels as well as the concentration of K in the soil solution. Very few soils have a homogeneous clay mineral content nor uniform particle size, and thus one specific K release rate is very unlikely. This was recognized by Mortland (1961) and Smith et al. (1971). Mortland found that K release and fixation can occur simultaneously in a system containing a heterogeneous group of 2:1 minerals not in equilibrium with each other and

Smith and co-workers determined that curves for soil K release merely represent the combined effects of the various particle sizes in the soil and not a distinctive mode of release. When cropping Mg-saturated soil clays Doll et al. (1965) found that larger amounts of K were removed from the coarse clay fractions (0.2-2.0 μ) than from the finer clay fraction (<0.08 μ) with intermediate amounts from the medium fraction (0.08-0.2 μ). In contrast, by relating the K content of the various clay size fractions and the relative amount of that fraction to the amounts of nonexchangeable K released, Arnold and Close (1961) concluded that neither the amount of the coarse clay (0.3-2.0 μ) nor its K content was necessarily related to the K supplying power of the soils. By using a Mg-saturated clay, Doll et al. were able to put much more stress on the lattice K and, as has been discussed earlier, the coarse fractions will continue to release K under higher stress conditions while the finer fractions will not. In support Evans and Attoe (1948) found that up to three times more nonexchangeable K was released from soils when the exchangeable K level was dropped by leaching with a $CaCl_2$-$MgCl_2$ solution before cropping. It seems that the amounts of K released depend upon the

exchangeable K level which acts as a "buffer" between the soil solution K and the K in the lattice of the clay minerals.

Although ammonium acetate extractions in the past have, in most cases, adequately provided a good prediction of the K release to plants, other methods of estimating K release for plant growth have been used. Potassium removal with successive salt extractions using 1 N NH_4OAc and 1 N NaCl-0.1 N HCl and a single NaOAc-NaTPB extraction were compared with K uptake by the Stanford and Dement cropping technique by Scott and Welch (1961). The concluded that the NaOAc-NaTPB solution removes the easily released K very quickly, that a crop can remove as much or more K if given enough time, and that successive NaCl-HCl extractions will also remove as much or more K due to the acid nature of the solution. Working with 9 soils, Schulte and Corey (1965) found that the best estimate of plant available K was the amount of K extracted from 2 g samples of nondried soil with 10 ml of 0.3 N NaTPB in 15 minutes ($r = 0.991$). The amounts of K extracted with NaTPB related to the K removed by 8 successive harvests of ryegrass over a 54 week period was nearly a 1:1 relationship.

METHODS AND MATERIALS

In August, 1970, a study was initiated in Peru to determine the relative availability of native soil K to plants and to study their K release patterns. Soils were screened in Peru by a cropping study and various laboratory measurements, and samples of selected soils were sent to Michigan State University (MSU) for more detailed studies.

Sampling Procedure and Supporting Data

Results from recent soil fertility experiments and from soil samples sent to the central soil testing laboratory in Peru were used to select sites which best represented the Peruvian sierra (mountains) with respect to area, agriculture and K content. A small number of jungle and coastal soils were included to provide a comparison of the K status of these different climatic regions with those of the mountains. Profile samples in which horizons were separated on the basis of color, texture and structure were obtained from 30 locations (Table 1, p. 33) distributed as follows:

6 from the northern sierra, 9 from the central sierra, 9 from the southern sierra, 4 from the jungle and 2 from the coast.

In Peru, soil pH was determined, using a 1:2.5 soil:solution ratio, with a glass electrode potentiometer. The Bouyoucus hydrometer method (Day, 1965) was used for texture measurements. A 1:5 soil:solution ratio and a 10 minute shaking period with 6 N H_2SO_4 was used to extract soil potassium, and K in solution was determined with a flame photometer. Organic matter estimates were obtained using the Walkley-Black wet combustion method with H_3PO_4 additions to sharpen the titration endpoint (Allison, 1965). Total exchangeable acidity was determined by extracting with 1 N KCl (1:10 soil:solution ratio) and titrating with 0.01 N NaOH (McLean, 1965). This information (Table 2, p.34) along with results from a short-term intensive cropping study was used to select 16 of the 30 soils for more detailed work at MSU. Five kg surface samples and 500 g subsurface horizon samples were steam sterilized by the Plant Quarantine Division of the USDA at Miami, Florida enroute to East Lansing.

At MSU the profile samples were routinely analyzed (Table 3, p.36) for pH in a 1:1 soil:water suspension with a

glass electrode potentiometer, and exchangeable K, Ca and Mg were extracted for 1 minute with 1.0 N NH_4OAc (pH 7.0), using a 1:8 soil:solution ratio. Potassium was determined on a Coleman flame photometer and Ca and Mg with a Perkin-Elmer 290 atomic absorption unit. Cation exchange capacities were determined by saturating the soil with Na using 1 N NaOAc pH 8.2, and then replacing the adsorbed Na with NH_4 as 1 N NH_4OAc pH 7.0 (Chapman, 1965). Sodium concentrations were determined using a Coleman flame photometer. Total carbon measurements on the surface samples were made with a Leco carbon analyzer. Data from 2 Michigan soils, a Kalamazoo sandy loam and a Sims clay loam, which were included in the study, are also given in Table 3, p. 36.

Soils with allophane or amorphous material present would be expected to have high exchangeable K levels, but a low capacity factor for K release. A test for allophane proposed by Fieldes and Perrott (1966) is based on the following reaction:

$$6\ NaF + Al(OH)_x \longrightarrow Na_3AlF_6 + 3Na + xOH^-$$

A production of hydroxyl ions causes a rapid pH rise above that of NaF (pH 7.9) which is good evidence for the presence of allophane. Twenty ml of 1 N NaF (saturated solution) was

added to 10 g soil samples, the mixture stirred, and pH determined after 30 sec, 1 min, 2 min, 4 min and 8 min time periods with a glass electrode potentiometer.

Soil Fraction Analysis

The sand, silt and clay fractions were separated for total K and X-ray analysis both during the initial phase of this study in Peru and after cropping at MSU. X-ray analyses of the clay fraction and total K contents of the clay and silt fractions before and after intensive cropping at MSU were used to evaluate changes in the clay mineralogy and the relative K contributions of the different soil fractions to plant growth.

Separation of soil fractions

Soil samples containing approximately 5 g (Peru) and 2 g (Michigan) of clay were exposed to various pretreatments to obtain a better separation of the soil fractions (Kunze, 1965). The soil samples were treated with 50 ml of 1 N NaOAc buffered to pH 5 with acetic acid and digested for 30 minutes at low heat on a hot plate to

dissolve carbonates and remove soluble salts. The suspension was filtered under suction and the filtrate discarded. The soil samples were then wetted with the NaOAc buffer and treated with successive increments of 30% H_2O_2 to destroy the organic matter. When there was no longer any apparent reaction with H_2O_2, the suspensions were centrifuged, the supernatant liquid discarded, and the sample warmed on a steam bath after addition of a solution of 40 ml of 0.2 M sodium citrate and 5 ml of 1 M $NaHCO_3$, in order to remove iron oxides. The suspension was heated to 75-80 C and 1 g of $Na_2S_2O_4$ added to reduce and solubilize the iron. After a 15-minute digestion period with frequent stirrings, the sample was centrifuged and washed 2 times with alcohol, each time discarding the supernatant. The samples were then dispersed by shaking 6 hours with either 200 ml Na_2CO_3 pH 9.5 (Peru) or 50 ml of a 5% Calgon solution (MSU). The sand fraction was removed by wet seiving with a 47 micron sieve before the clay and silt were separated in sedimentation cylinders, with settling time and sampling depth determined from a nomograph by Tanner and Jackson (1947). After separation the clays were flocculated with 1 $\underline{N}$ $MgCl_2$ and dried in a forced air oven at 80 C in Peru, and left in solution in Michigan.

X-ray analysis

X-ray analyses were made on the clay fractions of the soils before and after the intensive cropping at MSU to obtain estimates of the clay mineralogy of the soils and to determine any changes in the mineralogy by cropping. The Peruvian clays were treated for periods of less than 1 minute with an ultrasonic dispersion apparatus to obtain clay suspensions. To prepare oriented clay specimens, small amounts of clay suspension were placed on a porous plaster of paris block in a holder to which suction was applied. After each of the following treatments in the holder the clay specimens were X-rayed with a Norelco diffraction unit using Cu radiation: Mg saturated, glycerol solvated; K saturated, air dried; K saturated, heated to 300 C for 2 hr; and K saturated, heated to 550 C for 2 hr. The soil clays which were X-rayed after intensive cropping received only the Mg saturation, glycerol solvation treatment. Powder samples of several of the soil clays were prepared to obtain 060 spacings which were used to determine if the illite present was dioctahedral or trioctahedral.

Total potassium

Total K content of the whole soil and of the sand, silt and clay fractions was determined to estimate their relative contributions to the total. After intensive cropping, the silt and clay fractions were analyzed for total K to evaluate the relative K supplying ability of the two fractions.

Hydrogen peroxide (30%) was added to samples of soil (0.4 g), clay (0.1-0.3 g), silt (0.2 g) and sand (1.0 g) in Teflon[1] beakers to oxidize the organic matter. The samples were then treated with 0.5 ml concentrated H_2SO_4 and 5 ml HF, and placed on a sand bath at 200-220 C. After the samples were destroyed (in some cases more than one treatment was necessary) a 1:1 mixture of 6 N HCl and distilled water was added and heated to boiling to dissolve the residue. The samples were then taken to volume, and K in the solutions determined with a Coleman flame photometer.

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[1]Teflon is a DuPont trademark for polyfluoroolefin polymers.

Short-term Intensive Cropping

Intensive cropping studies were established in Peru at Huancayo (sierra) and La Molina (coast) with all 30 soils which were sampled to evaluate their short-term K supplying ability, and the 16 soils selected for further study were exhaustively cropped at MSU to determine K release patterns.

Cropping studies in Peru

For the studies in Peru, an amount of air-dry soil equivalent to 100 g of oven-dry soil was weighed in triplicate and mixed with amounts of $CaCO_3$ sufficient to neutralize the exchangeable acidity as measured by 1 N KCl (1.5 me Ca applied for each 1.0 me TEA). The samples were equilibrated at approximate moisture equivalent for 24 hr. Approximate moisture equivalent was determined by measuring the water content of the soil behind the wetting front in a beaker with an aeration tube to which water had been applied 24 hr previously.

After the incubation period, 100 g of acid-washed silica sand was added to each pot, the seeds planted (45 sorghum seeds at La Molina and 40 oat seeds at Huancayo),

covered with an additional 200 g of silica sand, and brought to approximate moisture equivalent with distilled water. The pots were maintained as closely as possible to this weight with daily additions of distilled water. Regular additions of Hoagland's minus K nutrient solution (Hoagland and Arnon, 1950) were added until a total of 400 ml had been added to each pot.

After cropping for 46 days at La Molina and 45 days at Huancayo, the plants were cut at sand level, dried at 70 C, weighed and ground to pass a 20-mesh sieve. Two-tenths gram of dry plant material was weighed and shaken for one hour with 50 ml 0.1 N HCl, filtered and diluted when necessary, and K in the filtrate determined with a flame photometer.

Cropping study in Michigan

At MSU, the 16 selected Peruvian soils and 2 Michigan soils were intensively cropped under controlled environmental conditions to better evaluate their K supplying ability and to determine K release patterns. Five separate croppings were made using a cropping procedure adapted from that described by Stanford and DeMent (1957).

Amounts of $CaCO_3$ to neutralize the milliequivalents of hydrogen present as determined by the SMP buffer method (Shoemaker et al., 1961) were equilibrated with triplicate 100 g samples of ovendry-equivalent soil. The soils were incubated in 16 oz wax cartons for three weeks during which time they were wetted to one-third bar moisture levels and allowed to air-dry four times. After incubation, the soils were placed in the growth chamber for cropping. The growth chamber was set to operate on a day period of 16 hr at 24 C and a night period of 8 hr at 18 C. The light intensity was 2,000 ft-candles at one-half canopy level. The relative humidity was maintained as nearly as possible above 50 percent.

Approximately 500 g of silica sand were added to 16 oz wax cartons into which another bottomless 16 oz carton had been inserted. Thirty oats seeds were evenly spread on the surface, all cartons brought to 750 g with additional amounts of silica sand, 80 ml distilled water added for germination and grown for 10 days in the growth chamber. During this time two 50 ml-increments of nutrient solution which did not contain K were added. The inside carton containing the oats seedlings with a mat of roots at the bottom was then removed and placed on top of the soils, also

in 16 oz waxed cartons, for a 14-day cropping period. After the transfer an amount of water was added equivalent to the one-third bar value plus 75 ml for the sand, and all cartons were adjusted to a uniform weight by adding more silica sand to facilitate daily moisture control. During the 24-day growing period, each carton received 200 ml of Hoagland's nutrient solution without K for the first and second cropping, and 250 ml of the same solution but with extra nitrogen for the third, fourth, and fifth cropping. Iron was added separately as FeEDDHA in 4 increments of 50 ml of a 5 ppm Fe solution to each crop.

After the mat of oats roots had been in contact with the soil for 14 days, the oats were harvested by cutting above the seed. No attempt was made to recover the roots from the soil. The layer of soil was separated from the sand, air dried and passed through a 4-mesh screen. Each soil carton was weighed so compensations for soil loss and sand and root gains could be made and the previously described steps repeated for the second, third, fourth and fifth oats crops.

The plant material was dried in a forced air oven at 65 C for at least 48 hr, weighed and ground to pass a

20-mesh sieve. Four-tenths g of plant material was shaken with 100 ml 0.1 N HCl for 1 hr, filtered and the concentration of K in the extract determined with a Coleman flame photometer.

On completion of the fifth harvest the soils were allowed to air dry and passed through a 2 mm sieve. Equal volumes of each replication were combined and mixed for total K and mineralogical analyses. Exchangeable K was determined on samples from each replicate.

Sodium Tetraphenylboron Extractions

Relative K removal rates and amounts of K which can eventually be removed by exchange reactions were determined using NaTPB as a precipitating agent for K. The method was essentially that of Smith and Scott (1966) in which 10 ml of 1.7 N NaCl was added to duplicate 1 g (O.D. equivalent) soil samples, and 1.02 g of solid NaTPB. The mixture was swirled and placed in a constant temperature cabinet (25 C) for 15 min, 1 hr, 10 hr, 100 hr, 1,000 hr and 2,000 hr time periods. When the time corresponding to the prescribed treatment had elapsed, 500 me of NH_4Cl and 6 mmole of $HgCl_2$

were immediately added. The sample was boiled for at least 20 minutes, cooled and filtered by suction. The solution was diluted to 1 liter and K in solution determined with a Coleman flame photometer.

Soil Solution Potassium Determination

Estimates of the concentration of K in the soil solution were made using a method described by Beckett (1964) for determining potassium activity ratios. Duplicate 5 g soil samples were equilibrated with 50 ml of solutions which were 0, 0.00025, 0.0005, 0.001 and 0.002 molar with respect to potassium (KCl) and 0.002 molar with respect to calcium ($CaCl_2$). The samples were shaken for 1 hr, allowed to stand for 12 hr, shaken for 30 min, filtered, and K in solution determined by flame photometry. The concentration of K in the initial solution which corresponded to no change after equilibration ($\Delta K = 0$) was used as an estimate of the concentration of K in the soil solution.

RESULTS

Soil fertility work in Peru has shown that the ability to predict responses to K fertilization is poor (McCollum and Valverde, 1968). To better characterize the potassium status of Peruvian soils, particularly those from the mountains, 30 soils were sampled and evaluated for K by cropping studies and laboratory measurements in Peru; 16 of these soils were selected and taken to MSU for more intensive studies.

Of the 30 soils originally sampled, 24 were from the mountains, with all except one at altitudes above 10,000 ft; slopes varied from 0 to 90% (Table 1). The two coastal soils were at altitudes of 300 and 400 ft with slopes of less than 1%, and the four jungle soils were at altitudes of 500 to 2,600 ft. with slopes varying from 0 to 100 percent.

The pH values of the soils sampled varied from 4.5 to 8.5 in the mountains, from 4.1 to 6.2 in the jungle, and from 8.2 to 8.4 on the coast; textures varied from clay to loamy sand (Table 2). Organic matter levels in these soils varied from 1.3 to 8.5% with no consistent

Table 1.--Location, altitude, stoniness, and slope of the soils at the 30 sites sampled in Peru.

Soil no.	Field	District	Province	Department	Altitude (ft)	Stones (%)	Slope (%)
1	Sulche Salto	Julcan	Otuzco	La Libertad	12,000	10	30-40
2	La Florida	Agallapampa	Otuzco	La Libertad	11,500	none	20-30
3*	Cahuadan	Huamachuco	Huamachuco	La Libertad	11,100	none	20-30
4*	Porcon	Cajamarca	Cajamarca	Cajamarca	11,700	none	15-20
5*	Carhuacunga	Cajamarca	Cajamarca	Cajamarca	11,100	0-5	30-40
6*	La Victoria	Cajamarca	Cajamarca	Cajamarca	9,700	0-5	0-5
7	Miraflores	Zurite	Anta	Cuzco	11,200	none	5-10
8*	Condebamba Nueva	Anta	Anta	Cuzco	10,900	3-6	0-5
9	Fierrohuasi	Anta	Anta	Cuzco	11,400	none	5-10
10*	Chaca Ccolla	Huarocondo	Anta	Cuzco	11,700	none	15-20
11	Queromarca	Tinta	Canchis	Cuzco	11,000	none	0-3
12*	Ichu	Puno	Puno	Puno	12,400	0-5	0-3
13	Tahuaco	Yunguyo	Chuchuito	Puno	12,450	0-5	2-5
14*	Yanamoco	Taraco	Huancane	Puno	12,200	10-15	3-5
15	Toccopujio	Capachica	Puno	Puno	12,400	0-1	5-10
16*	Santa Ana #24	El Tambo	Huancayo	Junin	10,700	none	0-3
17*	Yana Allpa	Heroinas T.	Concepcion	Junin	11,500	none	20-25
18	UNCP	El Mantaro	Jauja	Junin	10,800	none	0-5
19	INA 104	Huancani	Jauja	Junin	10,800	5-7	0-5
20	Chacayan	Sicaya	Huancayo	Junin	10,900	0-1	0-3
21*	La Ladrillera	Huachac	Huancayo	Junin	10,700	none	3-5
22	Ocshapampa	Chocon	Jauja	Junin	10,500	none	0-5
23	Nueve de Julio	Concepcion	Concepcion	Junin	10,700	15-20	0-3
24*	Hac. San Carlos	La Merced	Tarma	Junin	2,600	0-5	90-100
25	La Granja	Satipo	Satipo	Junin	2,200	0-1	0-3
26*	Comas	Comas	Concepcion	Junin	11,600	0-3	80-90
27*	Hac. San Isidro	Imperial	Canete	Lima	300	none	0-1
28*	EELM	Ate	Lima	Lima	400	0-1	0-1
29*	IVITA #7	Pucallpa	Coronel P.	Huanuco	1,800	none	4-8
30	IVITA BA	Pucallpa	Coronel P.	Huanuco	500	none	0-5

*Soils selected for further study at Michigan State University.

Table 2.--Chemical and physical determinations made in Peru on soil samples from 30 locations.

Soil number	pH	Texture (percent)			O.M. (percent)	Potassium (me/100 g)	Total exchangeable acidity (me/100 g)
		Sand	Silt	Clay			
1	5.1	53	22	25	4.2	0.92	2.40
2	4.5	33	28	39	3.2	0.37	3.80
3	5.0	75	10	15	2.3	0.57	1.65
4	5.0	63	24	13	8.5	1.03	5.55
5	6.9	55	22	23	2.0	0.43	0.10
6	8.1	43	26	31	4.1	0.62	0.00
7	8.1	33	30	37	7.1	0.30	0.00
8	6.9	55	20	25	3.5	1.65	0.00
9	6.3	43	28	29	3.3	0.83	0.10
10	6.0	31	38	31	2.5	0.57	0.20
11	8.5	9	34	57	2.2	1.00	0.00
12	6.9	79	14	7	1.3	0.32	0.05
13	5.9	63	22	15	2.4	0.58	0.15
14	7.2	59	26	15	1.7	0.37	0.05
15	5.6	37	44	21	4.9	0.63	0.10
16	5.8	39	28	33	2.8	0.22	0.20
17	4.9	27	36	37	4.7	0.50	1.25
18	6.4	11	20	69	3.8	0.40	0.10
19	8.0	39	32	29	4.3	0.50	0.00
20	8.1	31	34	35	2.2	0.75	0.00
21	6.0	41	30	29	2.1	0.45	0.10
22	4.5	43	29	28	2.0	0.33	1.70
23	7.0	55	20	25	2.8	0.40	0.05
24	6.2	63	20	17	4.1	0.18	0.10
25	6.0	65	22	13	3.1	0.47	0.20
26	6.8	55	24	21	3.1	0.75	0.05
27	8.4	45	34	21	2.0	1.38	0.00
28	8.2	45	26	29	2.1	0.77	0.00
29	4.3	47	26	27	1.8	0.20	5.60
30	4.1	27	33	40	4.1	0.38	8.10

differences apparent between the different areas. Amounts of K extracted with 6 N H_2SO_4 varied from 0.18 to 1.65 me/100 g; 12 of the 30 soils tested below 0.45 me/100 g. In 1969, (Fitts, 1969) K fertilizers were recommended for Peruvian soils testing below 0.41 me/100 g if the pH was 6.4 or lower and below 0.51 me/100 g if the pH was 6.5 or higher. Potassium chloride extractions for total exchangeable acidity ranged from 0 to 8.10 me/100 g with those soils having pH values at 5.0 or below containing the higher amounts.

Soil Chemical and Mineralogical Properties

Chemical measurements on soil horizons

To evaluate the uniformity of parent material and obtain an estimate of weathering, the pH, exchangeable K, Ca and Mg and cation exchange capacities were determined on profile samples from the 16 Peruvian soils (Table 3) selected for intensive studies in Michigan. Soil pH varied less than 0.5 units throughout the profile for the mountain soils 3, 4, 6, 10, 14 and 26, the coastal

Table 3.--Chemical measurements made in Michigan on 16 soil profile samples from Peru and 2 Michigan surface samples

Soil no.	Horizon depth (cm)	pH	Exchangeable cations (me/100 g) K	Ca	Mg	Cation exchange capacity (me/100 g)	Base sat. (%)	Organic matter (%)
			Peruvian soils					
3	0-20	4.4	0.35	0.88	0.16	9.46	14.7	1.77
	20-40	4.2	0.24	0.43	0.13	10.65	7.5	
	40-160	4.3	0.21	0.43	0.11	9.56	7.8	
	160-170	4.4	0.13	0.65	0.16	15.22	6.2	
4	0-35	4.7	0.94	6.07	1.29	70.11	11.8	13.27
	35-50	4.7	1.05	5.16	1.89	66.96	12.1	
	50+	5.1	0.93	2.45	0.77	37.83	11.0	
5	0-10	6.4	0.34	21.70	5.45	43.48	63.2	1.72
	10-50	6.1	0.16	19.33	4.52	46.96	51.1	
	50-100	6.2	0.18	21.71	4.99	51.74	51.9	
	100-120	6.6	0.18	23.86	4.92	43.48	66.6	
	120-140	6.8	0.22	31.88	5.86	42.60	89.1	
6	0-10	7.9	0.44	25.06	1.41	42.71	63.0	4.16
	10-20	7.8	0.38	27.73	1.11	39.56	73.9	
	20-40	7.9	0.26	22.66	0.94	26.96	88.5	
	40-120	8.0	0.32	21.71	0.88	21.96	104.3	
8	0-20	5.9	0.33	12.29	1.41	30.76	45.6	3.47
	20-40	5.7	0.27	12.52	1.41	32.39	43.8	
	40-75	6.7	0.40	12.52	1.89	28.48	52.0	
	75-125	6.7	0.26	13.45	2.11	30.87	51.2	
10	0-20	6.0	0.45	6.30	1.41	21.41	38.1	2.43
	20-80	6.0	0.53	9.51	3.88	36.63	38.0	
	80-140	6.4	0.56	12.52	4.84	37.39	47.9	
12	0-20	6.4	0.13	6.08	0.77	9.78	71.4	1.11
	20-40	6.4	0.16	6.76	1.09	15.22	52.6	
	40-90	6.9	0.09	2.45	0.41	6.52	45.2	
	90-170	7.3	0.09	2.22	0.32	5.43	48.4	
	170-220	5.7	0.38	12.75	1.92	37.61	40.0	
14	0-30	7.0	0.13	7.22	1.18	15.00	56.9	1.55
	30-45	7.5	0.11	7.68	0.66	15.87	53.2	
	45-60	7.4	0.10	6.08	0.60	14.35	47.2	
	60-110	7.4	0.14	7.67	1.14	16.52	54.2	
	110-160	7.1	0.14	8.36	2.20	18.70	57.2	

Table 3 (continued)

Soil no.	Horizon depth (cm)	pH	Exchangeable cations (me/100 g) K	Ca	Mg	Cation exchange capacity (me/100 g)	Base sat. (%)	Organic matter (%)
			Peruvian soils					
16	0-30	5.6	0.15	9.51	1.62	23.59	47.8	2.65
	30-55	6.7	0.20	11.82	2.33	24.56	58.4	
	55-110	6.6	0.17	10.66	1.95	24.13	53.0	
	110-145	6.9	0.21	11.82	2.14	30.43	44.8	
17	0-15	5.0	0.42	2.90	0.72	23.91	16.9	4.29
	15-35	5.1	0.35	2.23	0.74	24.78	13.4	
	35-70	5.3	0.35	3.13	1.20	22.17	21.1	
	70-120	5.4	0.30	4.48	1.71	18.70	34.7	
	120-180	5.6	0.23	4.71	1.98	21.96	31.5	
21	0-15	6.1	0.40	9.05	2.23	25.54	45.7	1.90
	15-50	6.5	0.68	17.43	8.12	43.91	59.7	
	50-110	7.7	0.58	13.68	4.52	29.78	63.1	
	110-155	7.7	0.87	21.71	10.16	31.74	103.1	
	155-185	7.9	0.37	19.37	3.01	18.15	125.1	
	185-190	7.7	0.54	22.19	3.14	26.96	95.9	
24	0-30	6.3	0.10	9.51	0.86	23.91	43.8	3.69
	30-140	7.1	0.09	9.28	1.44	17.93	60.3	
	140+	7.1	0.09	10.43	2.68	23.48	56.3	
26	0-30	6.5	0.21	6.08	0.66	15.65	44.4	2.95
	30-65	6.3	0.15	3.80	0.60	12.61	36.1	
	65-125	6.5	0.17	3.80	0.57	11.74	38.7	
	125-185	6.5	0.14	4.71	0.80	13.48	41.9	
27	0-25	8.0	0.71	13.45	1.14	18.70	81.8	1.64
	25-45	8.1	0.37	12.52	0.63	12.93	104.6	
	45-75	8.0	0.36	19.33	1.95	29.13	74.3	
	75-90	8.0	0.37	13.22	1.98	19.56	79.6	
	90-180	8.1	0.16	3.80	0.66	6.63	69.7	
28	0-20	7.9	0.42	13.68	0.77	26.30	56.5	1.72
	20-40	7.9	0.32	10.90	0.54	20.00	58.8	
	40-95	7.5	0.25	11.13	0.83	20.65	59.1	
	95-125	7.4	0.23	11.59	0.88	22.83	55.6	
	125-185	7.4	0.17	9.05	0.68	17.17	57.6	
29	0-5	4.0	0.23	0.88	0.35	20.65	7.1	1.69
	5-18	4.2	0.16	0.65	0.16	18.59	5.2	
	18-29	4.2	0.14	0.43	0.11	19.24	3.5	
	29-45	4.5	0.14	1.33	0.13	19.35	8.3	
	45-90	4.3	0.17	0.43	0.11	18.59	3.8	

Table 3 (continued)

Soil no.	Horizon depth (cm)	pH	Exchangeable cations (me/100 g) K	Ca	Mg	Cation exchange capacity (me/100 g)	Base sat. (%)	Organic matter (%)
			Michigan soils					
31*	0-20	7.1	0.42	2.21	1.47	12.50	32.8	1.18
34	0-20	6.0	0.48	11.90	3.17	40.11	38.8	6.37

*31, Kalamazoo sandy loam; 34, Sims clay loam.

soils 27 and 28, and the jungle soil 29. Soil pH increased with depth in soils 5, 8, 16, 17 and 21 (mountain) and 24 (jungle), and first increased and then decreased for soil 12 (mountain). Exchangeable K levels decreased with depth in soils 3, 5, 6, 17 and 26 from the mountains, 27 and 28 from the coast and 29 from the jungle, increased with depth for the mountain soil 10, remained relatively constant in soils 14 and 16 (mountain) and 24 (jungle) and were variable throughout the profile in soils 4, 8, 12 and 21 (mountain).

Intensive weathering as indicated by a low percent base saturation could be inferred for northern mountain soils 3 and 4 and jungle soil 29; however, the cation exchange capacity was much higher in soil 4 than in soils 3 and 29 (Table 3). An increase in pH and percent base

saturation with depth in the soil profile would indicate moderate weathering, which probably is the case for mountain soils 5, 8, 10, 16, 17 and 21 and the jungle soil 24. The remaining soils: 6, 12, 14 and 26 from the mountains and 27 and 28 from the coast appear to be relatively unweathered, however, only 12 and 26 were not calcareous.

Total potassium in surface samples

Soil samples and samples of the sand, silt and clay fractions were treated with H_2SO_4 and HF to destroy silicates to determine total K in the 16 Peruvian and 2 Michigan soils. The clay and silt fractions were also analyzed for total K after intensive cropping to measure any changes in the K content of these fractions during cropping.

The amounts of total K in the Peruvian soils varied from 0.15 to 3.97 percent K (Table 4). In general, the K contents of soils from the northern mountains were lower than those of other soils, with a K range from 0.15 to 0.86 percent. These soils are thought to be of volcanic origin which may explain the low values (Zavaleta, 1969). Of the 18 soils studied, 5 soils (3, 4, 5 and 6

Table 4.--Total potassium content of the entire soil and of the sand, silt and clay fractions before cropping and of the silt and clay fractions after cropping of 16 Peruvian and 2 Michigan soils.

Soil no.	Potassium concentration in percent					
					After cropping	
	Soil	Sand	Silt	Clay	Silt	Clay
3	0.15	0.02	0.10	0.95	0.11	0.65
4	0.47	0.80	0.68	0.34	0.68	0.26
5	0.86	1.21	1.19	0.34	1.02	0.37
6	0.70	0.65	0.50	1.59	0.36	1.36
8	1.46	1.52	1.61	1.33	1.28	1.33
10	2.22	1.66	2.44	2.97	2.32	2.23
12	1.45	1.20	2.04	2.18	1.95	2.15
14	3.02	3.29	2.39	4.16	2.19	4.05
16	2.04	1.67	1.84	3.36	1.45	3.15
17	1.71	1.32	1.35	2.46	1.13	2.56
21	1.17	0.69	1.29	1.58	1.19	1.32
24	2.29	2.38	2.19	2.59	1.90	2.41
26	3.97	4.03	2.50	3.25	3.61	3.55
27	2.01	1.82	1.91	2.07	1.71	1.85
28	1.91	1.64	1.73	2.82	1.65	2.49
29	0.27	0.03	0.07	1.00	0.07	0.82
31	1.15	1.08	1.86	1.19	1.75	1.25
34	1.92	0.51	2.01	2.41	1.98	2.93

from the mountains and 29 from the jungle) had total K contents lower than 1%, 7 soils (8, 12, 17 and 21 from the mountains, 28 from the coast and 31 and 34 from Michigan) contained between 1 and 2% K, and 6 soils (10, 14, 16 and 26 from the mountains, 24 from the jungle, and 27 from the coast) had amounts of K greater than 2%. Ten

of the 18 soils studied had total K levels higher than those reported by Olivera et al. (1971) who found total K contents ranging from 1,780 to 14,200 ppm in soils from southeastern Brazil which were classified as Oxisols, Ultisols, Alfisols, Mollisols and Inceptisols.

Total K contents of the sand, silt and clay fraction were variable with many soils containing different relative amounts in the various fractions. The amounts of K in the sand were the most variable with a range from 0.02 to 4.03 percent. The ranges of total K in the silt and clay were 0.07 to 2.50% and 0.34 to 4.16%, respectively. The K content increased as the particle size decreased for mountain soils 3, 10, 12, 16, 17 and 21, coastal soils 27 and 28, jungle soil 29, and Michigan soil 34, indicating some weathering has taken place on these soils. For mountain soils 4 and 5 the K content decreased as the particle size decreased which infers that the K present in these soils is mainly in primary minerals in the larger particles and not in the clay minerals. The K in the remaining soils was well distributed among the 3 fractions except for soil 6 which had substantially more K in the clays than in the sand and silt fraction.

The K content of the clay and silt fractions was in most cases lower after cropping than before cropping. Soils 3, 10 and 21 (mountain), 28 (coast), and 29 (jungle) appeared to have lost more K from the clay than the silt fraction, while mountain soils 5, 8, 14, 16 and 17 and jungle soil 24 had more K loss from the silt than the clay. These are trends only and statistically there was no overall significant difference at the 0.05 level of significance between K content in the silt or clay before and after cropping.

Clay mineralogy of surface samples

Sodium fluoride test for allophane: The presence of allophane or amorphous material was estimated by reacting 10 g soil samples with 20 ml 1 N NaF (pH 7.9) and measuring the increase in pH after 30 sec, 1 min, 2 min, 4 min and 8 min time periods (Fieldes and Perrott, 1966). A rapid pH rise was considered to be a positive test for the presence of allophane. The above authors state that the only likely exceptions of the above test are soils initially high in alkali or containing free $CaCO_3$ in

which a reaction occurs with NaF to precipitate CaF_2 and yield Na_2CO_3.

The pH values of the NaF-soil mixtures at different times after contact are given in Table 5. Soils 4, 6, 27, 28 and 31 all had pH values greater or equal to 9.3 at 2 min; however, the presence of free carbonates was noted in soils 6, 27, and 28 by effervescence with 3 N HCl. Positive evidence for the presence of allophane exists only for soils 4 (mountain) and 31 (Michigan). The presence of allophane is suspected in the mountain soils 5, 10 and 21 since the pH did increase to 9.0 at the 2 min time period.

X-ray analysis: The X-ray diffraction patterns of the oriented clay samples after various treatments are given in the Appendix. The interpretation of these patterns and the results of the NaF quick test for amorphous material are presented in Table 6. There is very little illite present in the soils from the northern sierra (3, 4, 5 and 6). Soil 3, a red soil which appeared to be highly weathered, contains mostly metahalloysite and amorphous material. The dominating clay mineral in soil 5 is montmorillonite. Soils 6 and 12 did not show a

Table 5.--pH values in a 1:2 soil:solution ration of N NaF (pH 7.9) after 0.5, 1, 2, 4 and 8 minutes for 16 Peruvian and 2 Michigan soils.

Soil no.	pH				
	0.5 min	1 min	2 min	4 min	8 min
3	8.4	8.6	8.7	8.8	8.9
4	9.3	9.4	9.5	9.6	9.6
5	8.9	9.0	9.0	9.1	9.1
6	10.0	10.1	10.1	10.2	10.2
8	8.2	8.2	8.2	8.4	8.4
10	8.8	8.8	9.0	9.1	9.2
12	8.5	8.5	8.6	8.7	8.8
14	8.7	8.8	8.8	8.9	9.0
16	8.0	8.1	8.1	8.2	8.3
17	8.4	8.6	8.7	8.9	9.0
21	8.9	9.0	9.1	9.2	9.3
24	7.9	7.9	8.0	8.1	8.3
26	8.4	8.5	8.6	8.7	8.7
27	10.0	10.1	10.1	10.2	10.2
28	9.9	10.0	10.0	10.1	10.1
29	8.4	8.5	8.6	8.7	8.8
31	9.2	9.3	9.4	9.5	9.6
34	7.9	7.9	8.0	8.1	8.2

Table 6.--Qualitative estimates of the clay minerals in 16 Peruvian and 2 Michigan soil clays.

Soil no.	Clay minerals
	Peruvian soils
3	Metahalloysite; some 2:1 intergrade material; quartz
4	Metahalloysite; allophane; small amounts of illite and vermiculite
5	Dioctahedral montmorillonite; vermiculite; illite; small amounts of quartz
6	Randomly interstratified montmorillonite, illite, and vermiculite; small amounts of kaolinite and quartz
8	Small amounts of montmorillonite; 2:1 intergrades; quartz
10	Illite; metahalloysite; quartz; feldspar
12	Randomly interstratified illite, chlorite, and montmorillonite; metahalloysite; small amounts of quartz and feldspars
14	Illite; randomly interstratified chlorite and vermiculite; metahalloysite; quartz
16	Illite; metahalloysite; vermiculite; quartz; feldspar
17	Metahalloysite; illite; quartz; feldspar
21	Small amounts of illite and metahalloysite; amorphous material; quartz; feldspar
24	Illite; metahalloysite; vermiculite; montmorillonite; quartz; feldspar
26	Dioctahedral and trioctahedral illite; metahalloysite; vermiculite; quartz; feldspar
27	Illite; kaolinite; montmorillonite; chlorite; randomly interstratified chlorite and montmorillonite; quartz; feldspar
28	Illite; kaolinite; chlorite; randomly interstratified chlorite, vermiculite, and montmorillonite; quartz; feldspar
29	Metahalloysite; randomly interstratified montmorillonite, illite and chlorite; quartz
	Michigan soils
31	Kaolinite; vermiculite and chlorite randomly interstratified with smaller amounts of illite; quartz; amorphous material
34	Illite; kaolinite; randomly interstratified vermiculite, chlorite and montmorillonite; quartz

dominating clay mineral species, but rather some 1:1 material and a random interstratification of montmorillonite, illite and either vermiculite (6), or chlorite (12). Metahalloysite, illite, quartz and some feldspars were present in mountain soils 10, 17 and 21; soils 10 and 21 contain some amorphous material, and soil 8 probably also contains some amorphous material even though it did not give a positive NaF test.

Soils 14, 16 and 26 from the mountains and soil 24 from the high jungle all contained metahalloysite, illite, quartz and some vermiculite; however, 14 appeared to have smaller amounts of chlorite randomly interstratified with the vermiculite. Soil 24 also contained montmorillonite. The illites in soil 26 appear to be predominantly dioctahedral; however, 060 spacing indicates the presence of some trioctahedral species. The presence of feldspars was indicated by peaks in the 3.18 Å range for soils 16, 24, and 26. The mineralogy of the two coastal soils, 27 and 28 is heterogeneous but similar with illite, kaolinite, chlorite, quartz, and feldspars present in both soils. Soil 27 also has a distinct montmorillonite component as well as montmorillonite randomly interstratified with chlorite while soil 28 has montmorillonite randomly

interstratified with chlorite and vermiculite. Metahalloysite is the dominant clay mineral with small amounts of randomly interstratified montmorillonite, illite and chlorite for the jungle soil number 29. Soil 31, a Michigan soil, contains kaolinite, amorphous material, quartz, and a random interstratification of chlorite, with smaller amounts of illite. Illite, kaolinite, quartz and randomly interstratified vermiculite, chorite and montmorillonite are the components of the clay fraction of soil 34, the other Michigan soil included in this study.

Short-term Intensive Cropping

Adaptations of the cropping method of Stanford and DeMent (1957) were used to evaluate the K supplying ability of Peruvian soils. Thirty soils were sampled and cropped in Peru in pot studies at 2 locations differing in climate and altitude. Results of these studies together with laboratory measurements were used to select 16 of the 30 soils for more rigorous cropping and laboratory studies at MSU.

Cropping studies in Peru

Dry matter yields, K concentration, and K uptake data from small pot intensive cropping experiments conducted on the coast at La Molina and in the mountains at Huancayo are given in Table 7. The dry matter yields were consistently lower, K concentrations higher, and K uptake generally higher in the mountains than on the coast, due partly to unusually cool and cloudy weather on the coast. At both locations the pots were outside; however, the pots at Huancayo were below a corrugated, clear plastic roof. The relationship between K uptake at the two locations and K extracted by neutral, normal ammonium acetate and 6 $\underline{N}$ H_2SO_4 are given as correlation coefficients in Table 8. With the more desirable growing conditions at Huancayo it made little difference if ammonium acetate ($r = 0.625$) or sulfuric acid ($r = 0.627$) was used to predict K uptake. Potassium extracted with ammonium acetate ($r = 0.532$) related better than that extracted with sulfuric acid ($r = 0.394$) to K uptake in the experiment on the coast. Of the above correlations none can be considered particularly good.

Table 7.--Yields (g/100 g soil), concentration of K in plant material (%), and K uptake (me K/100 g soil) of sorghum grown at La Molina and oats grown at Huancayo in a short-term cropping study of 30 Peruvian soils.

Soil no.	La Molina			Huancayo		
	Yield (g)	K concentration (%)	K uptake (me)	Yield (g)	K concentration (%)	K uptake (me)
1	2.21	1.24	0.69	0.99	2.91	0.73
2	1.83	0.52	0.25	0.91	1.59	0.37
3*	0.94	0.70	0.17	0.90	1.67	0.38
4*	2.24	0.86	0.49	1.42	2.68	0.97
5*	1.58	0.62	0.25	1.12	1.66	0.47
6*	1.76	0.49	0.22	1.18	1.59	0.48
7	0.99	0.46	0.11	1.26	0.92	0.29
8*	1.55	0.60	0.24	1.09	1.48	0.41
9	2.23	0.75	0.43	0.99	2.06	0.52
10*	2.82	0.58	0.42	1.10	1.77	0.50
11	1.92	0.62	0.30	1.14	2.46	0.72
12*	0.88	0.67	0.15	0.81	1.09	0.23
13	1.80	0.54	0.25	0.97	1.84	0.45
14*	1.71	0.66	0.29	0.98	2.79	0.71
15	1.52	0.76	0.29	1.17	2.42	0.72
16*	1.91	0.72	0.35	0.70	1.61	0.29
17*	1.92	1.05	0.52	1.04	1.50	0.40
18	2.18	1.05	0.59	0.62	1.89	0.30
19	1.09	0.65	0.18	1.08	1.40	0.39
20	2.86	0.62	0.46	1.21	2.24	0.69
21*	2.39	0.30	0.18	1.08	1.43	0.39
22	2.06	0.34	0.18	1.07	1.27	0.35
23	1.36	0.36	0.12	0.80	1.33	0.26
24*	1.85	0.31	0.15	0.97	1.20	0.30
25	2.53	0.47	0.30	1.16	1.87	0.55
26*	2.54	1.04	0.68	1.16	4.60	1.22
27*	1.69	1.05	0.45	1.34	3.78	1.28
28*	1.59	0.63	0.25	1.15	1.75	0.52
29*	1.24	0.31	0.08	0.99	0.83	0.21
30	1.65	0.39	0.16	0.51	1.41	0.18
Ave	1.83	0.64	0.31	1.03	1.90	0.51

*Soils selected for further study at MSU.

Table 8.--Correlation coefficients showing the relationship between various K extractants and K uptake by cropping.

	Uptake (Huancayo)	Uptake (La Molina)	NH_4OA (Peru)[c]
H_2SO_4 (Peru)	0.627**	0.394	0.718**
NH_4OA_c (Peru)	0.626**	0.532*	---
Uptake (La Molina)	0.644**	---	---
NH_4OA_c (Mich)	---	---	0.953**

*Significant at 0.05 level.
**Significant at 0.01 level.

Sixteen of the 30 soils were selected on the basis of variations in K uptake, location, exchangeable K level, and distribution of K in the profile for further cropping and laboratory studies at MSU.

Cropping study in Michigan

The 16 Peruvian soils and 2 Michigan soils were intensively cropped using the Stanford and DeMent technique to evaluate the release of K to plants. Five successive oat crops were grown on the soils with the mat of oat roots being in contact with the soil for 14 days for each cropping period.

Dry matter yields of the oats tops (Table 9) varied from 1.79 to 2.33 g for the 1st harvest and from 0.94 to 1.54 g for the 5th harvest. When the dry matter yields from the sand checks without soil were subtracted, the total accumulated dry matter yields varied from 1.54 to 3.98 g per 100 g soil, which corresponds to 15.4 to 39.8 tons per Ha. Soil 29, a weathered jungle soil, produced the least and soil 27, a relatively unweathered soil from the coast, produced the most dry matter. Dry matter yields from each soil, although still slowly decreasing, appeared to be similar for harvests 3, 4 and 5.

Concentrations of K on a dry matter basis in the oats tops from 5 successive crops (Table 10) varied from 0.59 to 2.80% in the first harvest and from 0.38 to 1.16% for the 5th harvest. DeMent et al. (1959) considered young oat plants containing 0.58% or less K to be extremely K deficient. Broeshart and Van Schouwenburg (1961) also reported K contents of 0.54% in 18 day old oat plants as being in the low range. There were only 2 soils, 26 (mountain) and 27 (coast), which produced oats plants in the 5th crop that had K concentrations substantially higher (1.16 and 0.87%, respectively) than these deficient levels. The

Table 9.--Yields of each of five successive two-week oat crops grown on 16 Peruvian and 2 Michigan soils.

Soil no.	Grams of dry material per 100 grams soil					
	First crop	Second crop	Third crop	Fourth crop	Fifth crop	Total
3	1.90*	1.39	1.23	1.08	0.94	6.54
4	2.26	1.66	1.45	1.24	1.16	7.77
5	2.04	1.60	1.48	1.30	1.23	7.65
6	2.08	1.63	1.50	1.48	1.28	7.97
8	1.94	1.54	1.31	1.19	1.18	7.16
10	2.06	1.65	1.39	1.37	1.29	7.76
12	1.79	1.46	1.21	1.04	1.01	6.51
14	2.17	1.68	1.43	1.28	1.35	7.91
16	1.86	1.47	1.24	1.06	1.02	6.65
17	1.91	1.48	1.24	1.09	1.05	6.77
21	2.11	1.55	1.35	1.29	1.30	7.60
24	1.82	1.52	1.31	1.04	1.07	6.76
26	2.15	1.79	1.67	1.47	1.54	8.62
27	2.31	1.79	1.60	1.57	1.52	8.79
28	2.14	1.58	1.45	1.43	1.42	8.02
29	1.83	1.35	1.17	1.03	0.97	6.35
31	2.08	1.41	1.26	1.08	1.05	6.88
34	2.33	1.57	1.44	1.38	1.43	8.15
Sand	1.04	1.03	0.97	0.88	0.89	4.81

*Average of these replications.

Table 10.--Concentration of potassium in each of five successive two-week oat crops grown on 16 Peruvian and 2 Michigan soils.

Soil no.	Percent potassium in dry matter				
	First crop	Second crop	Third crop	Fourth crop	Fifth crop
3	0.85*	0.39	0.39	0.41	0.40
4	1.97	0.69	0.43	0.47	0.42
5	0.99	0.60	0.46	0.46	0.43
6	1.08	0.81	0.63	0.61	0.52
8	1.03	0.58	0.47	0.57	0.49
10	1.03	0.72	0.50	0.51	0.46
12	0.60	0.47	0.42	0.47	0.45
14	1.45	1.01	0.67	0.72	0.60
16	0.82	0.60	0.50	0.52	0.44
17	0.90	0.50	0.47	0.50	0.46
21	0.91	0.61	0.48	0.47	0.44
24	0.65	0.50	0.51	0.56	0.47
26	2.07	2.05	1.50	1.20	1.16
27	2.80	1.82	1.06	0.93	0.87
28	1.23	0.80	0.56	0.66	0.59
29	0.59	0.39	0.40	0.43	0.41
31	0.94	0.50	0.41	0.43	0.38
34	1.78	1.17	0.60	0.72	0.63
Sand	0.29	0.29	0.35	0.35	0.33

*Average of three replications.

K concentrations in the oats tops for each soil were essentially the same for harvests 3, 4 and 5.

Amounts of K in the oats tops removed from the soils computed as mg K per 100 g soils are given in Table 11. Uptake of K in the first harvest varied from 10.7 to 64.5 mg K/100 g soil and from 3.8 to 17.8 mg K/100 g soil in the 4th harvest. In most cases the uptake of K in the 2nd harvest was usually one-half that of the 1st harvest, except for mountain soils 4 and 26 which had K uptake values in the 2nd harvest which were 25 and 75%, respectively, of the 1st harvest. Total K uptake determined by adding K content of all 5 crops and subtracting K content of plants grown without soil (check pots with sand only) for each of the 5 harvests show that K removed in the oat tops varied from 13.8 to 126.4 mg K/100 g soil, which is equivalent to removing from 276 to 2527 kg K per Ha (2,000,000 kg) from the soil.

The uptake of K, as determined from dry matter yields and K concentrations, for each soil was very similar for the last 3 harvests. These patterns are shown in figures 1, 2, 3 and 4 where cumulative uptake is plotted against time and with each time period corresponding to a separate cropping. Cumulative K uptake from the soils

Table 11.--Potassium uptake from five successive two-week oat crops grown on 16 Peruvian and 2 Michigan soils.

Soil no.	Milligrams potassium per 100 grams soil					
	First crop	Second crop	Third crop	Fourth crop	Fifth crop	Total uptake
3	16.19*	5.36	4.83	4.43	3.80	19.2
4	44.44	11.45	6.27	5.77	4.82	57.4
5	20.21	9.58	6.73	5.99	5.25	32.4
6	22.54	13.17	9.38	9.00	6.71	45.4
8	20.06	8.90	6.20	6.77	5.82	32.4
10	21.29	11.77	6.94	6.98	5.98	37.6
12	10.73	6.91	5.02	4.91	4.57	16.8
14	31.50	16.92	9.59	9.12	8.12	59.9
16	15.25	8.77	6.24	5.48	4.53	24.9
17	17.13	7.38	5.78	5.62	4.78	25.3
21	19.19	9.48	6.42	6.08	5.74	31.5
24	11.76	7.58	6.70	5.80	5.05	21.5
26	44.29	36.78	25.16	17.54	17.83	126.2
27	64.48	32.53	16.94	14.62	13.16	126.4
28	26.34	12.56	8.16	9.37	8.44	49.5
29	10.87	5.20	4.71	4.44	3.96	13.8
31	19.54	7.01	5.20	4.58	3.98	24.9
34	41.54	18.42	8.68	9.93	9.03	72.2
Sand	2.96	2.98	3.37	3.09	2.96	0

*Average of three replications.

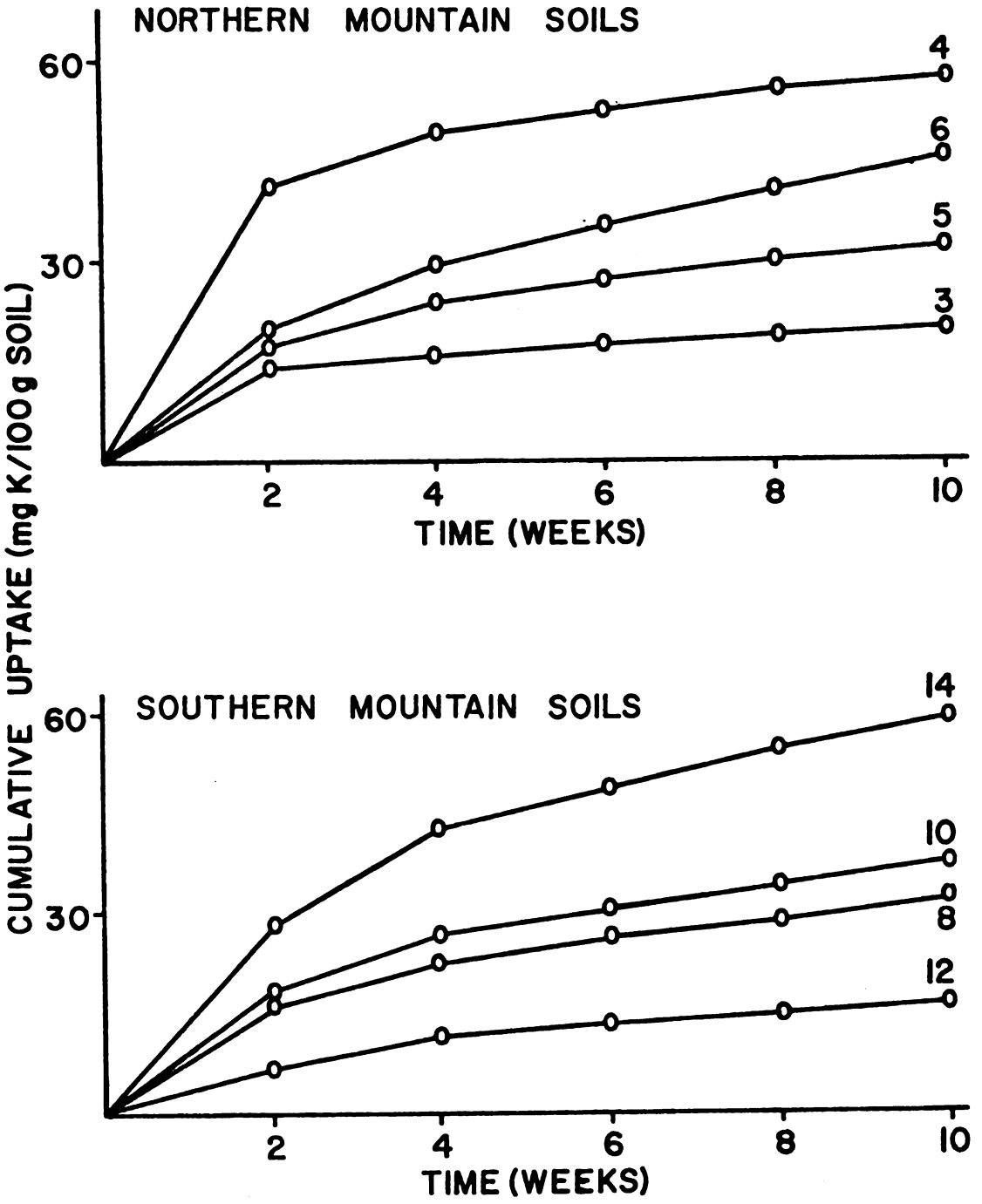


Fig. 1.--Cumulative uptake of potassium by five successive two-week oat crops grown on soils from the northern and southern mountain areas of Peru.

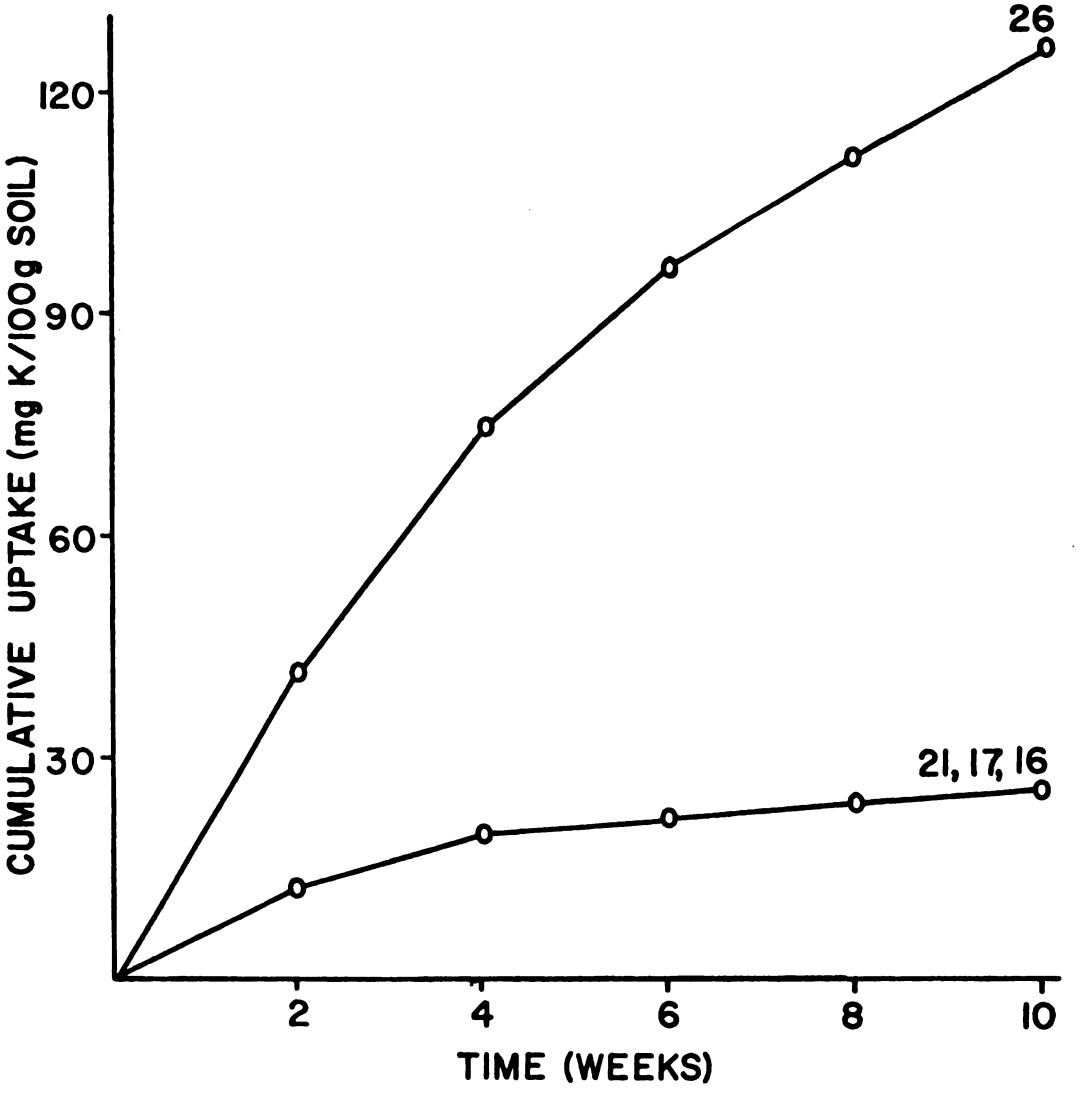


Fig. 2.--Cumulative uptake of potassium by five successive two-week oat crops grown on soils from the central mountain region of Peru.

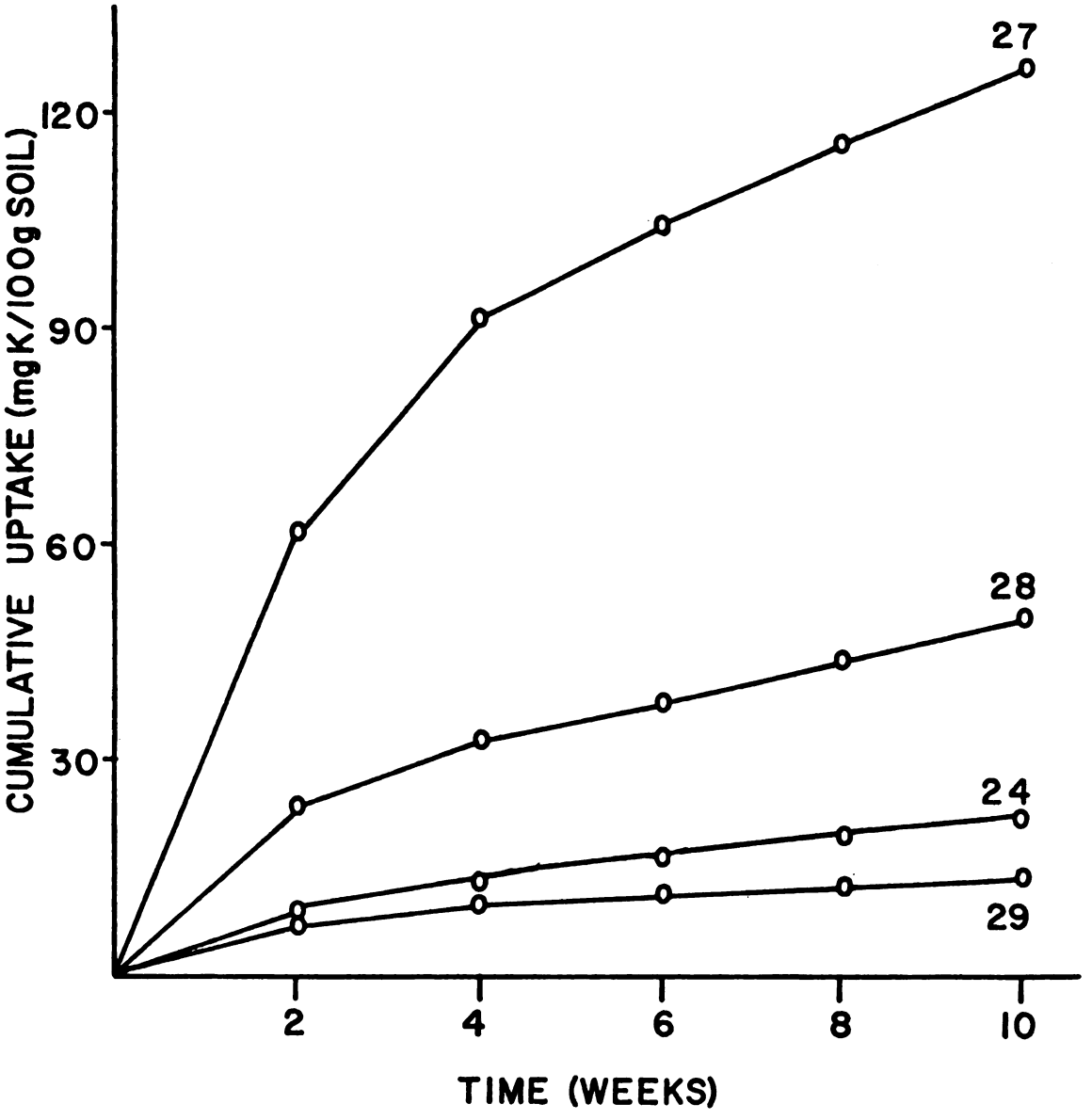


Fig. 3.--Cumulative uptake of potassium by five successive two-week oat crops grown on soils from the coastal (27 and 28) and jungle (24 and 29) regions of Peru.

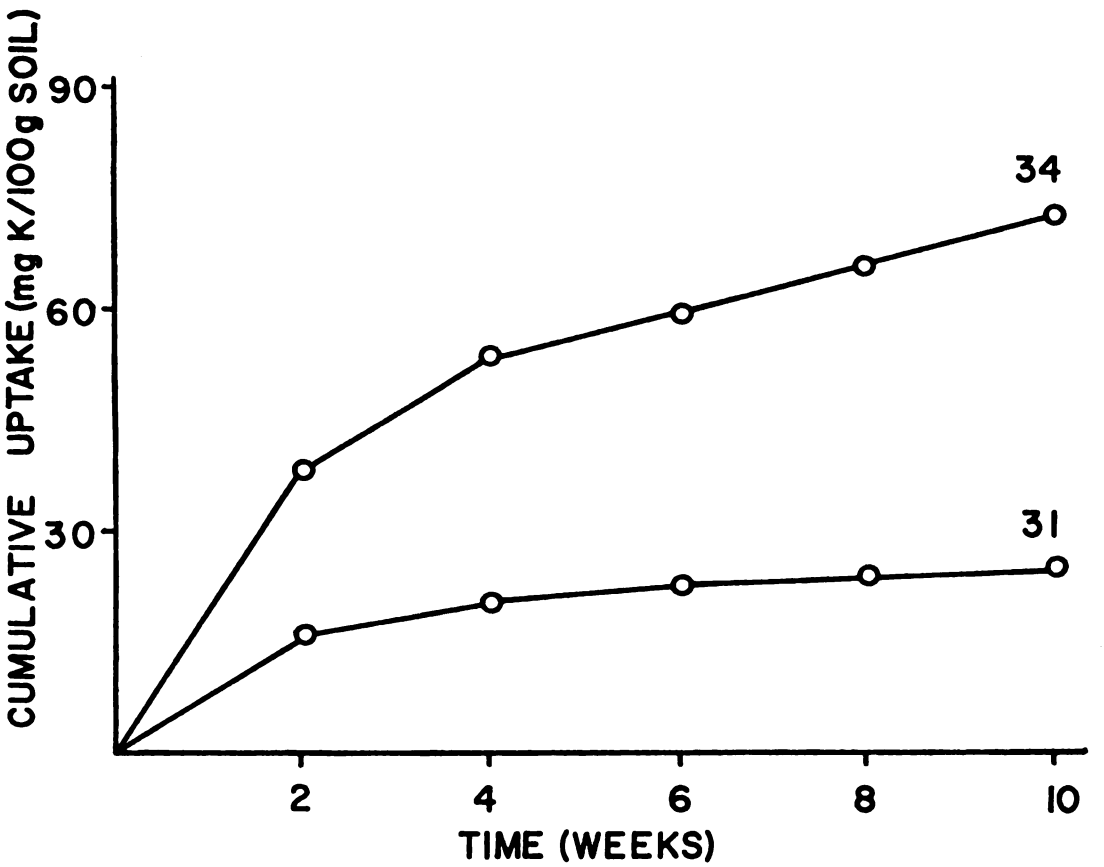


Fig. 4.--Cumulative uptake of potassium by five successive two-week oat crops grown on two Michigan soils.

from the northern and southern mountain regions are given in Figure 1, the central mountain region in Figure 2, the coast and jungle areas in Figure 3, and from Michigan, Figure 4. Since there appeared to be a linear relationship between cumulative uptake and time between 4 and 10 weeks, the slopes of the linear regressions were calculated for each soil during this period. The slopes or rate of K release as me K per 100 g soil per week are given in Table 12, together with coefficients of determination for each slope (linear regression coefficient). With one half of the coefficients of determination above 0.90 (90% of the variability in K uptake is explained by increasing the time of cropping), it appears that these slopes may give an estimate of the rate of release of K to plants over time. The highest K release rates of 0.1501 and 0.2146 me K/100 g/week were obtained from soils 27 (coast) and 26 (mountain) respectively while 0.0157 and 0.0159 me K/100 g/week from soils 3 (mountain) and 29 (jungle) were the lowest. More than a tenfold difference in rates of K release from soils cropped intensively with oats may be expected from these soils.

Table 12.--Linear regression coefficients expressed as rate of K release and corresponding coefficients of determination computed from accumulated uptake data for the 2nd, 3rd, 4th, and 5th oat harvests from 16 Peruvian and 2 Michigan soils.

Soil no.	Rate of K release (me/100 g/week)	Coefficient of determination (R^2)
3	0.0157	0.689
4	0.0321	0.633
5	0.0365	0.962
6	0.0676	0.863
8	0.0410	0.961
10	0.0452	0.973
12	0.0218	0.863
14	0.0746	0.965
16	0.0292	0.640
17	0.0291	0.969
21	0.0377	0.817
24	0.0347	0.901
26	0.2146	0.941
27	0.1501	0.949
28	0.0715	0.970
29	0.0159	0.624
31	0.0186	0.604
34	0.0787	0.882

The exact mechanism controlling K release is difficult to determine, since mass flow, diffusion and root interception are probably not occurring in the same relative proportions as was outlined by Barber (1962). In this case mass flow is probably more important in supplying K to plants since daily additions of water were made. Since the roots are in constant contact with the soil, root interception may be more important in supplying K to the plants and the roots can act as a more efficient sink for K removal. However, diffusion within the soil particles will probably ultimately determine K uptake. More discussion of these rates of release will be given in a later section.

Exchangeable K levels before and after cropping, K removal by cropping from exchangeable and nonexchangeable forms and K uptake as a percent of the total K are given in Table 13. Potassium removal from exchangeable forms was calculated as the difference between the ammonium acetate extraction before and after cropping; nonexchangeable K removal was determined as the difference between total K uptake by plants and the decrease in exchangeable K due to cropping. Exchangeable K levels of the different soils were decreased from 0.04 to 0.82

Table 13.--Exchangeable K levels before and after 5 successive croppings and uptake of soil K expressed as total K uptake, % of total K in soils and % of K uptake derived from exchangeable and nonexchangeable sources when 16 Peruvian and 2 Michigan soils were intensively cropped in a growth chamber.

Soil no.	Exchangeable K (me/100g)		Uptake of soil potassium					
			Total uptake (me/100g)	Percent of total K	Exchangeable		Nonexchangeable	
	Before cropping	After cropping			K (me/100g)	Percent of total K uptake	K (me/100g)	Percent of total K uptake
3	0.35	0.06	0.49	12.5	0.29	59	0.20	41
4	0.94	0.12	1.47	12.2	0.82	56	0.65	44
5	0.34	0.11	0.83	3.8	0.23	28	0.60	72
6	0.44	0.27	1.16	6.5	0.17	15	0.99	85
8	0.33	0.15	0.83	2.2	0.18	22	0.65	78
10	0.45	0.15	0.96	1.7	0.30	31	0.66	69
12	0.13	0.08	0.43	1.2	0.05	12	0.38	88
14	0.13	0.09	1.53	2.0	0.04	3	1.49	97
16	0.15	0.06	0.64	1.2	0.09	14	0.55	86
17	0.42	0.08	0.65	1.5	0.34	52	0.31	48
21	0.40	0.13	0.81	2.7	0.27	33	0.54	67
24	0.10	0.06	0.55	0.9	0.04	7	0.51	93
26	0.21	0.10	3.24	3.2	0.11	3	3.13	97
27	0.71	0.14	3.24	6.3	0.57	18	2.67	82
28	0.42	0.15	1.27	2.6	0.27	21	1.00	79
29	0.23	0.06	0.35	5.1	0.17	49	0.18	51
31	0.42	0.06	0.64	2.2	0.36	56	0.28	44
34	0.48	0.11	1.85	3.8	0.37	20	1.48	80

me/100 g by cropping, with the greatest decrease in exchangeable K with soil 4 (mountain) and least decrease with soil 24 (jungle). From 3 to 59% of the total K uptake by plants was from exchangeable K. For 8 of the 18 soils cropped, 20% or less of the total uptake came from exchangeable sources and for 14 of the 18 soils cropped, more than 50% of the net K uptake was from nonexchangeable K sources.

Potassium extracted by ammonium acetate would be a poor indication of K release to plants for those soils with low exchangeable K levels, but which released substantial amounts of K to plants. Mountain soils 14 and 26 had exchangeable K levels before cropping of 0.13 and 0.21 me/100 g soil respectively, but released 1.53 and 3.24 me/100 g to oats plants in 5 successive croppings with 97% of the net K uptake coming from nonexchangeable sources.

Of those soils from which more than one me of K was removed by cropping, soil 4 (mountain) was the only soil in which more than 50% of the total K uptake was from the exchangeable form. This soil had the highest initial exchangeable K level (0.94 me/100 g), but it decreased to 0.12 me/100 g after cropping. Soils 3 and 17

from the mountains, 29 from the jungle, and 31 from Michigan also furnished substantial amounts of K to oats plants from exchangeable forms. From mountain soils 3, 4 and 6, coastal soil 27 and jungle soil 29, more than 5% of the total K was removed by intensive cropping, with 12.5 and 12.2 percent being removed from soils 3 and 4, respectively. Soils such as these will require frequent K fertilizer additions to avoid K deficiencies.

The K extracted by neutral, normal ammonium acetate was correlated with the total uptake of K by oats plants for each of the five harvests. As the soils were successively cropped, the correlations between initially exchangeable K and the K taken up by plants decreased as is shown by a decrease in the correlation coefficients from 0.693 to 0.388 (Table 14). The importance of nonexchangeable K when intensively cropping soils is shown by the correlation coefficient of 0.973 between total uptake of K by plants and the uptake of nonexchangeable K. The relationship between K uptake from the first cropping and K removal from nonexchangeable forms was higher ($r = 0.793$) than that for K removed from exchangeable sources ($r = 0.667$), indicating the importance of K from nonexchangeable forms even at the beginning of intensive

Table 14.--Correlation coefficients between accumulated net uptake of K after each of 5 successive crops and exchangeable soil K before and after cropping, and uptake of exchangeable and nonexchangeable soil K by oats grown on 16 Peruvian and 2 Michigan soils.

Accumulated net uptake by harvest	Exchangeable K		Uptake Sources	
	Before cropping	After cropping	Exchangeable K†	Nonexchangeable K††
1	.693**	.263	.667**	.793**
1,2	.535*	.264	.498*	.914**
1,2,3	.457*	.258	.417	.950**
1,2,3,4	.423	.268	.377	.963**
1,2,3,4,5	.388	.265	.342	.973**

† Uptake of exchangeable K = Exchangeable K before cropping - Exchangeable K after cropping.

††Uptake of nonexchangeable K = Total K uptake - Uptake of exchangeable K.

*Significant at 0.05 level.

**Significant at 0.01 level.

cropping. Indications from this study are that for soils which will be intensively cropped, ammonium acetate will not suffice to extract amounts of K which will be related to uptake. Most field crops, however, will not remove the large amounts of K from a soil that was removed here by intensive cropping and ammonium acetate in general has adequately predicted K uptake under field conditions.

Sodium Tetraphenylboron Extractions

Sodium tetraphenylboron (NaTPB) when employed as a precipitating agent for K insures that the K in solution will be at a low level (Ksp KTPB = 2.24×10^{-8}; Geilmann and Gebauhr, 1953). With low K levels in solution, diffusion of K from the interlayers of illites and micas increases in an attempt to establish equilibrium. Sodium ions are added to the mixture so that they may replace the K ions diffusing out and thus maintain electrical neutrality in the clay mineral. One g soil samples were allowed to stand with 10 ml of solutions which were 0.3 M NaTPB and 1.7 M NaCl at constant temperature (25 C) for 0.25, 1, 10, 100, 1,000 and 2,000 hr time periods to determine rates of K release and the total amount of K which could be removed by exchange reactions.

The amounts of K which were precipitated as KTPB from 16 Peruvian and 2 Michigan soils for different time periods are given in Table 15. After the 15 min exposure time, the amounts of K released from the soils ranged from 0.8 to 4.4 me/100 g with the unweathered coastal soil (27) releasing the most and 2 soils from the northern mountains (3 and 5) releasing the least. Compared to 15

Table 15.--Potassium extracted (me/100 g) from 16 Peruvian and 2 Michigan soils by solutions containing sodium tetraphenylboron for different time periods.

Soil no.	Extraction time (hours)						Percent of total soil K removed (2000 hr)
	0.25	1	10	100	1000	2000	
	me K/100 g						
3	0.8	1.0	1.7	2.7	2.9	2.8	73.2
4	1.9	2.2	2.5	4.1	3.7	3.8	31.9
5	0.8	1.1	1.7	1.8	1.5	1.9	8.7
6	2.3	3.2	4.3	5.9	6.2	6.9	38.5
8	4.1	4.1	5.6	6.6	7.3	7.4	19.9
10	1.9	2.5	4.3	7.5	9.0	9.5	16.7
12	1.2	1.4	3.1	5.9	6.0	6.4	17.2
14	2.7	4.9	20.5	48.3	64.3	66.9	86.6
16	1.8	2.5	5.0	17.6	36.2	38.5	73.8
17	1.7	1.7	4.9	12.8	20.3	21.0	47.9
21	1.8	1.9	2.9	3.6	4.3	4.3	14.5
24	1.4	1.4	3.7	8.2	14.1	16.4	27.9
26	2.5	4.2	11.7	26.2	45.0	52.2	51.4
27	4.4	5.4	8.9	14.3	18.8	18.9	36.8
28	3.3	5.4	11.4	17.5	18.7	19.6	40.1
29	1.1	1.0	1.6	2.7	3.7	3.3	48.0
31	1.8	1.3	1.9	2.9	4.8	4.9	16.5
34	3.9	5.9	11.5	18.7	21.2	23.7	48.2

min there was a small increase in the range of amounts of K extracted during the 1 hr time period (1.0 to 5.9 me/100 g). After 10 hr most of the soils which were to eventually release large amounts of K could be recognized, namely mountain soils 14 (20.5 me/100 g) and 26 (11.7), coastal soils 27 (8.9) and 28 (11.4) and the Michigan soil 34 (11.5). At 10 hr soil 29, a weathered jungle soil, had released the least amount of K (1.7 me/100 g). Soils 16 and 17 (mountain) and 24 (jungle) also were to release substantial amounts of K but did not show an indication of their releasing ability until the 100 hr time period when they released 17.6, 12.8 and 8.2 me/100 g, respectively. At this time period the mountain soil 14 had released the most (48.3 me/100 g) and soil 5 the least K (1.8 me/100 g). Soils 3, 4, 5, 6, 8, 12 and 21 (mountain) and 29 (jungle) released less than 1.0 me/100 g from 100 hr to 1000 hr and thus during this time period had essentially reached their maximum capability to supply K. Amounts of K which could be expected from these soils by exchange reactions varied from 1.5 to 6.2 me/100 g soil. After 1000 hr as after 100 hr, mountain soil 14 released the greatest amount of K (64.3 me/100 g). For the mountain soils 10 and 17, the coastal soils 27 and

28, and the Michigan soil 31, the release of K after 2000 hr as compared to 1000 hr was less than 1.0 me/100 g; thus after 2000 hr extraction time, 13 of the 18 soils had essentially stopped releasing K. Of the remaining soils 14, 16 and 26 (mountain), 24 (jungle), and 34 (Michigan), only soil 34 released as much K from 1000 to 2000 hr as it had from 100 to 1000 hr, and this was a low amount, 2.5 me/100 g. Soils 24 and 26 from the mountains released the most K of any of the soils, 66.9 and 52.2 me/100 g respectively, and soils 3 and 5, also from the mountains, released the least, 2.8 and 1.9 me/100 g respectively.

The percentages of the total soil K removed by precipitation with NaTPB from each soil after the 2000 hr extraction period are given in Table 15. Comparisons between the amount of K extracted after 2000 hr with NATPB and its percent of the total K indicate variations in K sources and release mechanisms. Mountain soils 3 and 16 both released approximately 73% of their total K after 2000 hr; however, soil 3 released only 2.8 me/100 g while 38.5 me/100 g was removed from soil 16. Although these soils both released a high percentage of their total K, there was a greater than tenfold difference in the amounts of K removed. Soils 5, 8, 10, 12 and 21 from the mountains, and 31 from Michigan were more consistent in that they all

released less than 10 me K/100 g which amounted to less than 20% of their total K. The low amounts of K removed and corresponding low percent of the total K indicates the presence of framework silicates which would release only small amounts of K by this method. There was considerable variation in the amounts of K (3.8, 6.9, 16.4, and 18.9 me/100 g) removed from the respective mountain (4 and 6), jungle (24), and coastal (27) soils even though the corresponding percentages of total K (31.9, 38.5, 27.9 and 36.8) were similar. Soils 17, 28, 29 and 34 whose respective locations were the mountains, coast, jungle and Michigan all released between 40 and 50% of their total K, and except for the jungle soil, the corresponding amounts of K removed (21.0, 19.6, 3.3 and 23.7 me/100 g) were also about the same. Thus, a substantial amount of the K found in these soils can be removed by exchange reactions. Those soils which released the largest amounts of their total K (soils 3, 14, 16 and 26) were all from the mountains of Peru. However, the 73.2 percent of the total K released from soil 3 was only 2.8 me/100 g. The 66.9 me K/100 g from soil 14 was the largest amount and the highest percent of the total K (86.6) removed of any of the soils in the study. The maximum K removed from soils by this

method reported by Smith et al. (1968) was 24.6 me/100 g which corresponded to 47% of the total K.

The relationships between amount of K extracted with NaTPB and logarithm of contact time are illustrated in figures 5 and 6. The three curves in Figure 5 represent 14 of the 18 soils which had similar release patterns. The mountain (3, 4, 5 and 21), jungle (29), and Michigan (31) soils represented by curve C, released K in low amounts and at a low rate. Larger amounts of K were released by mountain soils 6, 8, 10 and 12 as is shown by curve B; however, these soils also were slow releasers of K. Curve A represents soils 17 (mountain), 27 and 28 (coastal) and 34 (Michigan) and shows an overall faster release rate than either B or C. The soils represented by curve A would be expected to release moderate amounts of K until a maximum had been reached. There were no common release patterns noted for the remaining soils presented in Figure 6. It is apparent that soils 24 (jungle) and 26 (mountain) are still releasing K even after 2000 hr although the rate of K release is higher for soil 26 than for soil 24. The rate of K release from the mountain soils 14 and 16 is decreasing rapidly after high release rates which removed substantial amounts of K from these soils.

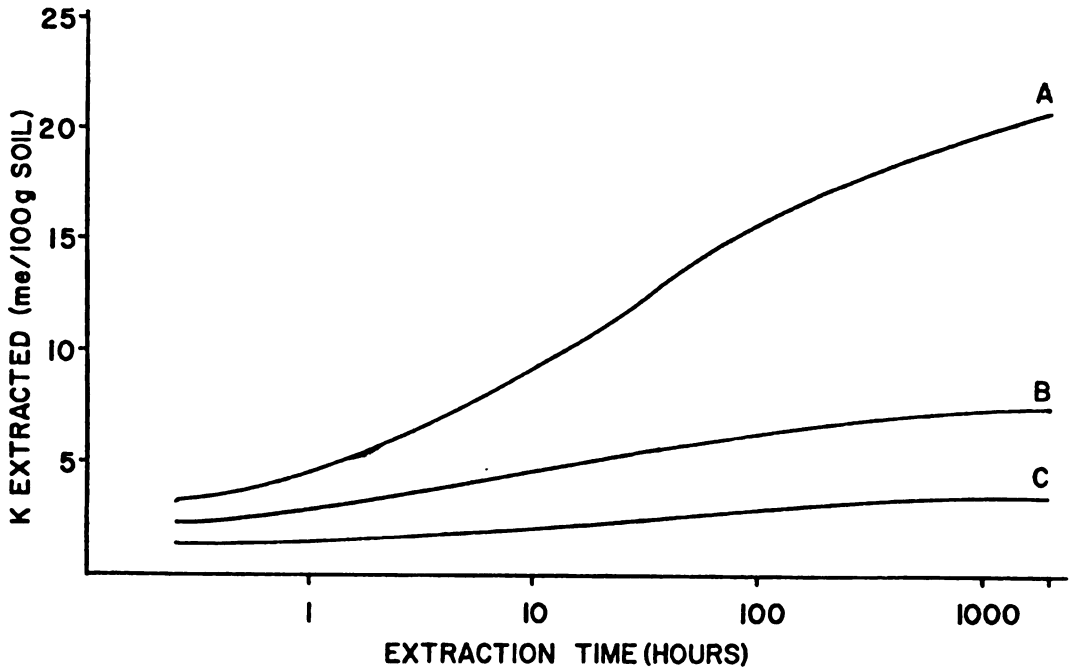
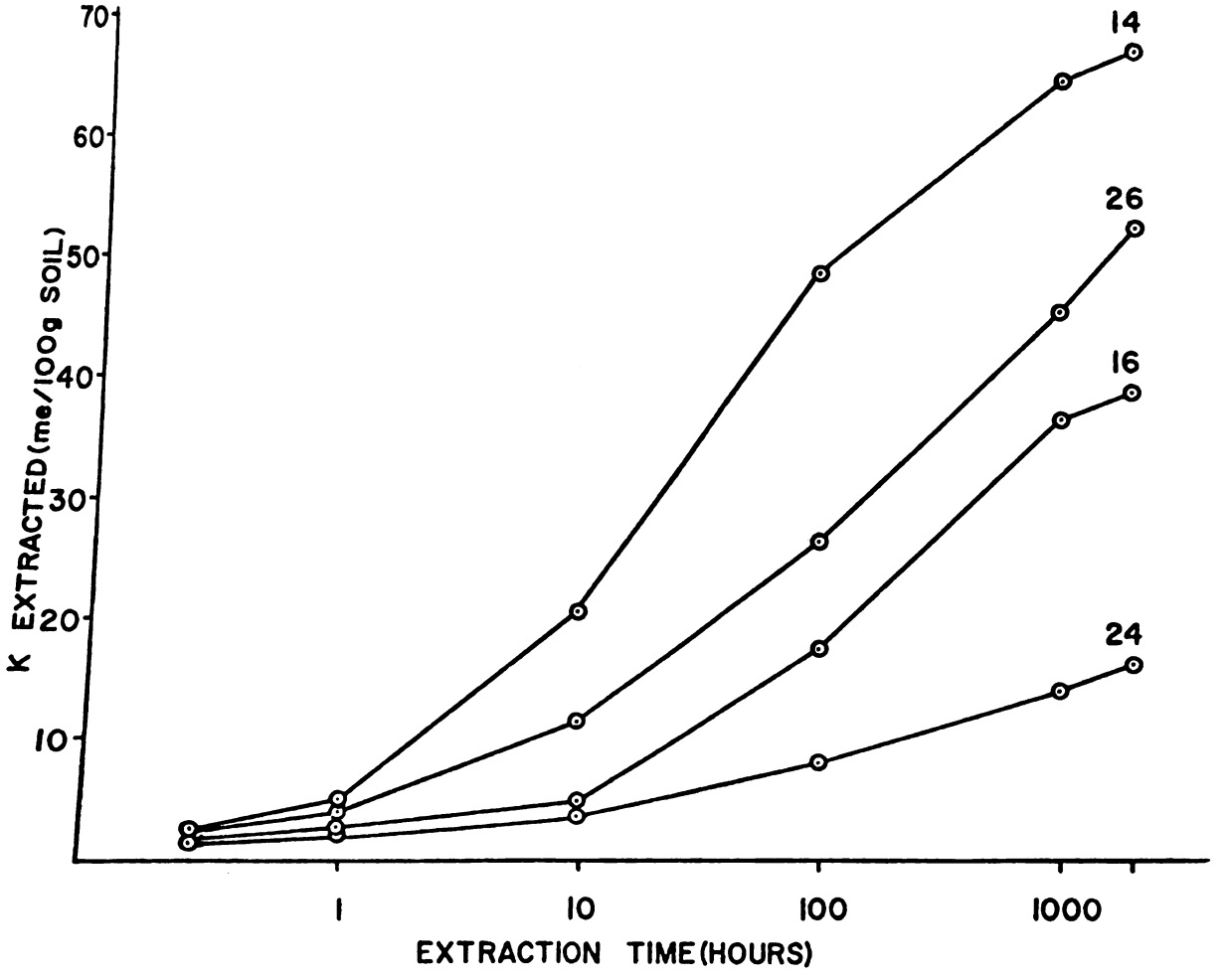
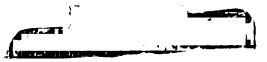


Fig. 5.--Potassium extracted from soils 17, 27, 28 and 34 (curve A), 6, 8, 10 and 12 (curve B) and 3, 4, 5, 21, 29 and 31 (curve C) with sodium tetraphenylboron for diffrent time periods.



ig. 6.--Potassium extracted from soils 14, 16, 24 and 26 with sodium tetraphenylboron for different time periods.



An extractable K rate index as suggested by Smith et al. (1968) was computed by dividing the difference in K removed from 10 to 1000 hr by the difference of the logarithms of the respective times. Although the units of these numbers would be me/100 g, they represent an average over a logarithmic scale and thus should be used only for comparative purposes among soils. It can be inferred from these numbers that soils 3, 4, 5, 6, 8, 12 and 21 from the mountains, 29 from the jungle, and 31 from Michigan are relatively slow K releasers, soils 10 and 17 from the mountains, 24 from the jungle, 27 and 28 from the coast, and 34 from Michigan will release K at a medium rate and K can be removed at a rapid rate from mountain soils 14, 16 and 26.

The K release during this same time period was also calculated as an average release rate of K (me K/100 g/wk) so that these rates (Table 16) could be compared with those obtained by cropping (Table 12). The coefficients of determination computed for linear regression equations (Table 16) computed with no logarithmic transformation of the time variable are indicators of the validity in using this average release rate for each particular soil. In most cases the fit of the regression

Table 16.--Rate indices, rate of K release, and coefficients of determination for linear regression equations describing removal of K from 16 Peruvian and 2 Michigan soils by solutions containing sodium tetraphenylboron in contact with soil samples for 10, 100 and 1000 hr periods.

Soil no.	Rate index 10-1000*	Average rate release 10-1000**	Linear R^2***	Linear R^2 Log****
		..(me K/100g/wk)..		
3	0.60	0.20	0.50	0.87
4	0.60	0.20	0.14	0.54
5	-0.10	-0.03	0.72	0.34
6	0.95	0.32	0.47	0.79
8	0.85	0.29	0.67	0.93
10	2.35	0.80	0.61	0.93
12	1.45	0.49	0.35	0.75
14	21.90	7.43	0.68	0.97
16	15.60	5.30	0.89	0.99
17	7.70	2.61	0.81	0.99
21	0.70	0.23	0.85	0.99
24	5.20	1.76	0.87	0.99
26	16.65	5.65	0.87	0.99
27	4.95	1.68	0.77	0.99
28	3.65	1.24	0.46	0.85
29	1.05	0.36	0.82	1.00
31	1.45	0.49	0.91	0.95
34	4.85	1.65	0.57	0.92

*Rate index = $\frac{\text{K extracted (1000 hr) - K extracted (10 hr)}}{\log 1000 - \log 10}$

**Average K release rate = $\frac{\text{K extracted (1000 hr) - K extracted (10 hr)}}{1000 - 10}$

***R^2 values for linear regression equation: me K = a+b(time) with time ranging from 10 to 1000 hr.

****R^2 values for linear regression equation: me K = a+b(log time) with time ranging from 10 to 1000 hr.

line to the data was much better with a logarithmic transformation of time. Smith et al. (1968) have reported a linear relationship between the amount of K extracted with NaTPB and the logarithm of the contact time for 16 Iowa soils. More discussion of these release rates will follow in another section.

Soil Solution Potassium Determinations

By equilibrating soil samples with solutions of varying K concentrations, an estimate of the soil solution K concentration can be obtained for that particular time. After equilibration the concentrations of K in solution are obtained and compared to the original concentration of the solution which was equilibrated with the soil sample. When plotting the difference in these two concentrations (ΔK) against the concentration of K originally in the solution, a linear relationship should be obtained. The point or K concentration where K is neither adsorbed nor released by the soil ($\Delta K = 0$) is considered to be the concentration of K in the soil solution. A value similar to this called the activity ratio was

computed by Beckett (1964) using the activities of K, Ca and Mg as $A_K/\sqrt{A_{(Ca + Mg)}}$ rather than the K concentration in the soil solution.

Values obtained by determining only the K concentration in solution are given in Table 17. The range in K concentrations from 3.7 to 72.0 ppm is in accord with values from 3 to 156 ppm found by Barber (1962) in the literature. Nine of the eighteen samples had values less than 10 ppm and fifteen were below 30 ppm. This is similar to the frequency distribution of the K concentration in the saturation extracts of 142 soils from the midwest of the United States (Barber et al., 1962).

Table 17.--The concentration of potassium (ppm K) in soil extracts after equilibration with solutions of varying potassium concentrations and the soil solution potassium concentration calculated from these data for 16 Peruvian and 2 Michigan soils.

Soil no.	Potassium concentration of initial solution (ppm K)					ppm K in soil solution
	0	10.4	20.5	40.7	84.4	
	...ppm K in solution after equilibration...					
3	11.2	18.6	27.5	44.7	82.8	72.0
4	19.1	23.0	27.3	36.3	61.5	32.8
5	5.5	8.7	12.2	19.5	36.4	8.0
6	2.7	5.5	7.6	14.3	30.5	3.7
8	4.1	8.3	11.6	20.3	38.9	6.9
10	5.1	10.0	15.0	25.7	50.3	9.6
12	2.2	8.6	15.0	28.4	64.0	5.8
14	2.5	7.7	12.5	22.3	45.0	5.0
16	2.2	8.0	11.3	20.4	36.3	5.0
17	8.2	13.8	20.7	33.5	68.5	21.0
21	4.0	7.5	12.7	22.3	46.1	6.0
24	2.1	7.7	14.7	26.9	59.5	4.5
26	6.0	11.9	19.3	33.6	70.5	16.0
27	15.6	19.7	25.5	37.1	68.0	32.2
28	5.9	10.5	15.8	26.3	50.6	10.6
29	7.2	14.4	22.3	36.9	76.0	27.0
31	7.5	14.0	21.0	34.9	72.5	27.2
34	5.7	11.0	15.6	24.8	47.2	11.5

DISCUSSION

The amounts and rates of release of K from the different soils are extremely variable as are the K removal rates within a soil when comparing short-term K release to the total K supplying power of a soil. The clay mineralogy and various chemical measurements are oftentimes helpful in explaining many of these differences.

Potassium Release Patterns of Soil Groups

Similarities in clay mineralogy and K release by cropping and NaTPB extractions were used to place the soils in several groups (Table 18). The soils which released comparatively low, medium, and high amounts of K will be considered first, second, and third, respectively.

Soils with low potassium supplying capabilities

Soils 3 and 29: Soil 29, a red, weathered jungle soil, and soil 3, a red, highly weathered mountain soil,

Table 18. -- Potassium status and K release characteristics of 16 Peruvian and 2 Michigan soils grouped according to release capabilities and clay minerals present in the clay fraction.

Soil no.	K removal by cropping		K removal by NaTPB			Soil K measurements			
	Total uptake	Rate of K release	2000 hr extraction		Rate of release from 10-1000 hr	Total Soil K	Exchangeable K		Soil Solution K
	(me K/100g)	(me K/100g/wk)	(me/100g)	Percent of total K	(me K/100g/wk)	(me/100g)	(me/100g)	(% of CEC)	(ppm)
.....Soils with low potassium supplying capabilities.....									
3	0.49	0.016	2.8	73.2	0.20	3.8	0.35	3.70	72.0
29	0.35	0.016	3.3	48.0	0.36	6.9	0.23	1.11	27.0
4	1.47	0.032	3.8	31.9	0.20	12.0	0.94	1.34	32.8
12	0.43	0.022	6.4	17.2	0.49	37.1	0.13	1.33	5.8
31	0.64	0.019	4.9	16.5	0.49	29.4	0.42	3.36	27.2
5	0.83	0.036	1.9	8.7	-0.03	22.0	0.34	0.78	8.0
8	0.83	0.041	7.4	19.9	0.29	37.3	0.33	1.07	6.9
21	0.81	0.038	4.3	14.5	0.24	29.9	0.40	1.57	6.0
6	1.16	0.068	6.9	38.5	0.32	17.9	0.44	1.03	3.7
10	0.96	0.045	9.5	16.7	0.80	56.8	0.45	2.10	9.6
.....Soils with medium potassium supplying capabilities.....									
27	3.24	0.150	18.9	36.8	1.68	51.4	0.71	3.80	32.2
28	1.27	0.071	19.6	40.1	1.24	48.8	0.42	1.60	10.6
34	1.85	0.079	23.7	48.2	1.65	49.1	0.48	1.20	11.5
16	0.64	0.029	38.5	73.8	5.30	52.2	0.15	0.65	5.0
17	0.65	0.029	21.0	47.9	2.61	43.7	0.42	1.76	21.0
24	0.55	0.035	16.4	27.9	1.76	58.6	0.10	0.42	4.5
.....Soils with high potassium supplying capabilities.....									
14	1.53	0.075	66.9	86.6	7.43	77.2	0.13	0.87	5.0
26	3.24	0.215	52.2	51.4	5.65	101.5	0.21	1.34	16.0

were very similar in their mineralogical and chemical properties. The K in exchangeable form in soil 3, although higher than that in soil 29 (0.35 and 0.23 me/100 g respectively) is not as strongly adsorbed as that in soil 29 as is indicated by soil solution K concentrations of 72 and 27 ppm and K saturation percentages of 3.70 and 1.11, respectively. Unpublished results of field experiments on soil 3 have shown an apparent response to Mg fertilizers; the high concentrations of solution K measured in this soil may have been a contributing factor to the development of Mg deficiency. This substantiates the need for cation balance studies for these weathered soils with low cation exchange capacities. Long term K release will be low, as is indicated by an extremely low K rate removal by cropping (0.016 and 0.016 me K/100 g/wk) and NaTPB (0.20 and 0.36 me K/100 g/wk) for soils 3 and 29, respectively, and is substantiated by low amounts of K bearing minerals in the clay fraction.

Soil 4: Low amounts of K would be expected to be released from this soil once the initial exchangeable K has been depleted. High soil solution K concentration

(32.8 ppm), a relatively high K saturation of the CEC (1.34%), and high exchangeable K (0.94 me/100 g) are reflected in a high initial K release to cropping which decreased rapidly after the second crop. Only small amounts of illite were present in the clay fraction and exchangeable K accounted for 7.8% of the total K in the soil. Regular monitoring of exchangeable K levels will probably be necessary and although this was not a liming study, adding lime to neutralize acidity due to Al (TEA = 5.5 me/100 g) should enable this soil to adsorb more exchangeable K since K has been found to compete more favorably with Ca than with Al for exchange sites (Mahilum et al., 1970).

Soils 12 and 31: Although there were differences in the clay mineralogy of these soils the chemical properties were similar: the K sources in soil 12, a mountain soil, were interstratified illite, montmorillonite, and feldspar and the K sources in 31, a Michigan soil, were vermiculite and amorphous material. Rates of K removal by cropping were similar for soils 12 (0.022 me/100 g/wk) and 31 (0.019 me/100 g/wk), although the K uptake varied (0.43 and 0.64 me/100 g) as did the exchangeable K (0.13

and 0.42 me/100 g) and the K in the soil solution (5.8 and 27.2 ppm), respectively. It appears that once the initial K levels are decreased by cropping as predicted by exchangeable and soil solution K the different K sources as indicated above would release K at similar rates. This is substantiated by the NaTPB extractable K which was 6.4 and 4.9 me/100 g and 17.2 and 16.5 percent of the total K for soils 12 and 31, respectively.

Soils 5, 8 and 21: Montmorillonite (5) and amorphous material (8 and 21) with their similar cation exchange capacities (∿100 me/100 g) appear to be the major contributors of exchange sites for K in these mountain soils. Short-term rates of release as indicated by cropping were low and almost identical for these 3 soils (0.036, 0.038, 0.041 me K/100 g/wk for soils 5, 21 and 8 respectively), although further K release would be expected to be much less from soil 5 than from soils 8 and 21 as is shown by the NaTPB extractions (-0.03, 0.29 and 0.24 me/100 g/wk). Low soil solution K levels of 8.0, 6.9 and 6.0 ppm and low to medium exchangeable K levels of 0.34, 0.33, and 0.40 me K/100 g for soils 5, 8 and 21, respectively, indicate that the amount of K which is

present on the exchange sites is tightly sorbed but that the equilibrium is rapid enough to supply K for low to moderate crop production. The sand and silt fractions contain more K than does the clay in soils 5 and 8 suggesting that major amounts of K in the soils is probably in primary minerals that would be expected to release only low amounts of K as is indicated by the above data. The K, although present in higher amounts in the clay in soil 21, is probably tightly held in the poorly structured illite. There was no response to added K fertilizer in a field experiment on soil 21 indicating that the amount of K removed by ammonium acetate (0.40 me/100 g) is an adequate level for crop production for this soil. A K saturation percentage of 1.57 which is about average for the soils in this study would indicate that K is competing favorably for the exchange sites. Thirty-three percent of the K uptake by cropping was due to exchangeable K forms. It would seem that a response to K fertilizer could be expected in the near future if crop production was maintained at a high level.

Soils 6 and 10: Potassium release patterns of the mountain soils 6 and 10 were similar as is noted by the K

release by cropping (0.068 and 0.045 me K/100 g/wk) and the NaTPB extractions (0.32 and 0.80 me K/100 g/wk, respectively). Similar exchangeable K values of 0.44 and 0.45 me/100 g corresponded to similar total uptake values of 1.16 and 0.96 me K/100 g even though the soil solution K values of 3.7 and 9.6 ppm from soils 6 and 10, respectively, were more variable. The 6.9 and 9.5 me of K removed with NaTPB accounted for 38.5 and 16.7 percent of the total soil K from soils 6 and 10, respectively. This variation can probably be explained by the feldspar detected in the clay fraction of soil 10. Both soils contained poorly structured illite which is probably the main source of the smaller amounts of K which diffused from the interlayers and this structural disorder may be such that the K-O bonds have been shortened which would make the K more difficult to remove.

Soils with medium potassium supplying capabilities

Soils 27, 28 and 34: Although the clay mineral makeup of these soils is very similar, a lower base saturation in the surface of the Michigan soil 34 (38.8%) indicates that this soil has been more intensely weathered

than the 2 Peruvian coastal soils 27 and 28, with their respective base saturations of 81.8 and 56.5%. Although soils 27, 28 and 34 all released similar amounts of K when treated with NaTPB (18.9, 19.6 and 23.7 me/100 g, respectively) which was 36.8, 40.1 and 48.2 percent of the total K, the soil solution and exchangeable K values were much higher for soil 27 (32.2 ppm and 0.71 me/100 g respectively) than for soils 28 (10.6 ppm and 0.42 me/100 g) and 34 (11.5 ppm and 0.48 me/100 g). This was reflected in the total K uptake and K release rates which were 3.24, 1.27 and 1.85 me/100 g and 0.150, 0.071 and 0.079 me K/100 g/wk for soils 27, 28 and 34, respectively. A liberal K fertilizer application to soil 27 in recent years would explain the above results. Since some of this K could have been fixed by the vermiculite, it would be more easily released as was shown by Mortland et al. (1957) than if the K had to come from illite.

These soils all have a fairly well ordered illite component and K contents in the clay fraction above 2 percent which would support the high amounts of K removed by NaTPB.

Soils 16, 17 and 24: Except for no vermiculite in soil 17 (central mountains) and the presence of montmorillonite in soil 24 (high central jungle) the clay mineralogy of these 3 soils is very similar. The percent K in the clay fraction (3.36%) was substantially higher, however, in soil 16 (central mountains) than in soils 17 (2.46%) and 24 (2.59%). Even though similar amounts of K were removed by cropping (0.64, 0.64 and 0.55 me/100 g from soils 16, 17 and 24 respectively) and the K release rates by cropping were similar (0.029, 0.029 and 0.035 me K/100 g/wk) the exchangeable (0.15, 0.42 and 0.10 me/100 g) and soil solution K (5.0, 21.0 and 4.5 ppm) levels were somewhat different. It may be that K fixed in vermiculite in soils 16 and 24 was not measured by the ammonium acetate due to a blocking effect by the ammonium ion but this K was available to plants when a concentration gradient was established by the plant root. There was evidently some trioctahedral illite present in soil 16 as this soil released 38.5 me K/100 g which was 73.8% of its total K. This is substantiated somewhat by a 060 X-ray spacing of 1.54 Å and a low second order (002) illite peak at 4.98 Å. Vermiculite, illite and feldspars were probably responsible for the lower, but substantial,

amounts of K removed by NaTPB from soils 17 (0.65 me/100 g) and 24 (0.55 me/100 g).

Soils with high potassium supplying capabilities

Soils 14 and 26: Potassium was released at high rates from these mountain soils which were similar in their clay mineralogy. NaTPB removed 66.9 me/100 g (86.6% of the total K) from soil 14 and 52.2 me/100 g (51.4% of the total K) from soil 26. When these soils were cropped, soil 14 released 1.53 me K/100 g and soil 26 released 3.24 me K/100 g. The rates of K removal were 0.075 and 0.215 me/100 g/wk by cropping and 7.43 and 5.65 me/100 g/wk with NaTPB for soils 14 and 26 respectively. The high amounts of K released by cropping were not indicated by the K concentration in the soil solution (5.0 and 16.0 ppm) nor the low exchangeable K levels of 0.13 and 0.21 me/100 g respectively, from soils 14 and 26. Both of these soils have good crystalline illite peaks and the presence of dioctahedral and trioctahedral species are indicated by a high second order illite peak and the 060 X-ray diffraction spacing, respectively. They appear to be relatively unweathered as is shown by base saturation percentages in

most cases above 50% throughout the profile. For soils such as these, ammonium acetate as a K extractant is not adequate to predict a yield response to applied K fertilizer.

Potassium Release Characterization

Most of the soils in this study released amounts of K that represented maximum quantities which could be expected to be released from the soil by surface and interlayer exchange reactions. Soils 24 and 26 were the only soils which were still releasing substantial amounts of K at the 2000 hr extraction period. In general, the amounts of K which these soils were capable of releasing was related to the clay minerals, specifically illite, present in the clay fraction.

Of the soils classified as having low K supplying capabilities (3, 4, 5, 6, 8, 10, 12, 21, 29 and 31) only soils 10 and 12 had X-ray diffraction patterns showing any illite present. This illite was very poorly structured as was indicated by low, broad 10 Å peaks. Thus, very little interlayer K is available for release and most of

the K must come from either primary or secondary minerals in the larger size fractions or from surface exchange sites. Smith et al. (1968) removed equal amounts of K (2.3 me/100 g) from <50μ orthoclase feldspar with NaTPB extractions for 1 day and 15 wk time periods which indicates that small amounts of K can be expected to be released from feldspar minerals. The soils in the low K supplying group, however, only released from 1.9 to 9.5 me/100 g at low rates varying from -0.03 to 0.80 me K/100 g/wk indicating that feldspars may be contributing substantial amounts of the total K removed, especially for the lower K releasers. A good relationship exists between the exchangeable K and the uptake of K from the first crop of oats for these 10 soils ($r = 0.979$). Thus for soils with none or low amounts of illite present, the surface-sorbed K is more important as a source of K for plant growth, and ammonium acetate should be an adequate extractant for removing K which is related to that taken up by plants.

Soils 16, 17, 24, 27, 28 and 34 were considered to have medium potassium supplying capabilities although soil 16 released amounts of K in the 2000 hr NaTPB extraction comparable to the amounts of K removed from the soils

considered to be high K releasers. The clay mineral illite present in all of these soils was much more crystalline as indicated by sharper and narrower peaks than that found in soils 10 and 12 of the previous group. In addition to better structured illite, vermiculite was also present in all of the soils except number 17 which also had the poorest illite structure. It is possible that this vermiculite is slowly forming as K in the illite is removed. After 1500 hr, Scott and Reed (1962) were able to remove from a Grundite illite 74 me/100 g with NaTPB which amounted to 68% of the total K present. The soils classified as medium in K supplying power released from 16.4 to 38.5 me K/100 g which amounted to 27.9 and 73.8% of the total K, respectively. This would suggest that K in the illite in the above soils was a major source of K removed by NaTPB. Due to the presence of this illite, these soils would probably be able to supply more K at a given exchangeable K level. In this group are 2 of 4 soils from the central mountains, the 2 coastal soils, and 1 soil each from the jungle and Michigan.

The two soils which were considered to have high K releasing capabilities had higher and sharper 10 Å peaks than any of the previous soils. Vermiculite was

also present, but in smaller amounts as was indicated by peak heights. These soils are probably much younger in age than the other soils and appear to be relatively unweathered. The K in this crystalline material, which may be mica, is much easier to remove as is shown by both cropping and NaTPB extractions. It appears that relatively small amounts of K need be removed to change some of this 10 Å material to vermiculite in soil 26 (Figure 7). Supporting evidence such as K fixing ability and cation exchange capacities are needed to substantiate this since only 3 me K/100 g were removed in the cropping experiment. This soil should release much larger amounts of K by cropping if more intensive methods such as those of Mortland et al. (1956) and Doll et al. (1965) were used.

When comparing the K removal by NaTPB and the appearance of the illite X-ray diffraction peaks, it appears that the more crystalline illites release K in larger amounts and at higher rates than those which are poorly structured. The diffusion of K out of the interlayers should be related to the crystallinity of the illite. Rich (1968) states that the type of bonding within the crystal structure, the extent and type of disorder within the crystal or at crystal terminations,

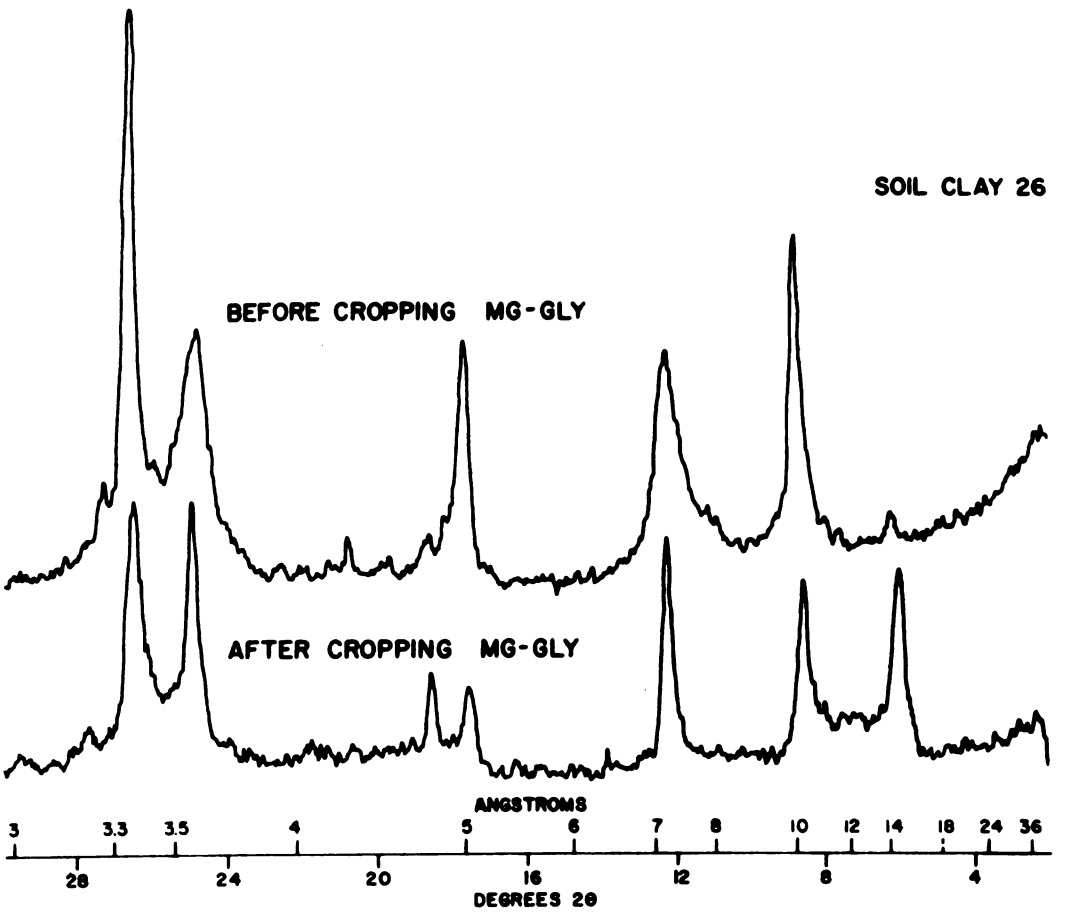


Fig. 7.--X-ray diffraction patterns of magnesium saturated, glycerol solvated clay from soil 26 before and after intensive cropping.

and crystal size are mineral properties that determine the rate at which weathering occurs and K is released.

There were no good relationships between soil solution, exchangeable, total or NaTB-15 min extractable K and the total K uptake by oats in 5 successive croppings. The lowest K removal of any of the soils was by jungle soil 29 (276 Kg/Ha) and in most cases the K removed was substantially higher than amounts which most field crops would be expected to remove in a cropping season. The relationship of exchangeable K was best with K uptake from the first crop. This would be expected since the exchangeable K is an important K source in the earlier stages of cropping. The concentration of K in the soil solution was not well related with either K uptake from the first crop or the total K uptake indicating the level of K in the soil solution is not a determining factor for uptake for these soils, but more important how fast the K in solution can be replenished. This is substantiated somewhat by a correlation between rate of K release by cropping and K uptake from the first crop of 0.751 and suggests that even at the first cropping, the rate of release or diffusion of K was influencing K uptake. The concentration of K in the soil solution was

somewhat related to the percent K saturation (r = 0.717) and to the total K in the soil (r = 0.786) indicating that the surface and inter-particle exchange sites for K do influence the level of K in solution to some extent.

The total K contents of the soils was not related to the K uptake by the first crop, but there appeared to be a relationship between total K in soils and K uptake by plants for the 2nd, 3rd, 4th and 5th crops, as shown by correlation coefficients of 0.662, 0.688, 0.687 and 0.714, respectively. Thus the total amount of K in the soil, most of which would be in the mineral form is related to K removal under intensive cropping conditions. This further substantiates the use of slopes of cumulative K uptake curves as indicators of the rate of K release by cropping from these soils.

The total K uptake was not as well related to the amount of K removed with NaTPB by 15 min extractions as has previously been shown by Schulte and Corey (1965) who reported a correlation coefficient of 0.991; however, their reported relationship between exchangeable K and K uptake by intensive cropping was also very good (r = 0.971). They also reported a 1:1 relationship between K uptake and the K removed with NaTPB after 15 min while

NaTPB in this study removed in many cases 3 times as much K from the Peruvian and Michigan soils as was removed by the 5 successive oats crops.

The intensive cropping experiment thus removed more K than what a field crop would be expected to remove and less than that with the 15 min NaTPB extraction. Thus some of these soils will release substantial amounts of K to NaTPB even at short time periods which would suggest that the surface-sorbed K is not always readily available to plant roots. As an example of this, soil 8 released 4.1 me/100 g to NaTPB in 15 min. but only 0.83 me to 5 oats crops. X-ray diffraction patterns for this soil indicated essentially no clay minerals present which suggests that much of the K available for plants must be surface adsorbed K. In contrast, soil 26 released less K with the 15 min NaTPB extraction (2.5 me/100 g) than was removed by the 5 oats crops (3.2 me/100 g). In this case well-crystallized illite, maybe mica, was indicated by X-ray diffraction analysis and the K removed probably was mainly lattice K since the exchangeable K was very low (0.21 me/100 g). With a 15 min extraction period the amount of K removed was limited by the rate of diffusion.which was not the case for cropping since a larger

time period permitted more K to diffuse from the clay mineral and thus the plant root could remove it.

With soils varying in mineralogy and therefore in K release mechanisms as these soils do, a simple extractant may not be adequate to evaluate the K status of these soils, with respect to plant-available K. Potassium extracted with ammonium acetate seems to relate well with the K release by soils which have small amounts of poorly structured illite present such as those in the first grouping; however, for these soils with well crystallized illite present, the K releasing capacity is not adequately evaluated.

SUMMARY AND CONCLUSIONS

Soil profile data, kinds of clay minerals, extractions with NaTPB, intensive cropping studies and exchangeable, soil solution, and total K determinations were used to evaluate the K status of 16 Peruvian and 2 Michigan soils. Variation in pH, exchangeable K, and percent base saturation through the soil profiles indicated that very few of the soils studied have been intensively weathered, On 1 mountain soil and 1 jungle soil the base saturation was near 10% and the pH values ranged from 4.0 to 4.5 through the profile indicating that they were the more intensely weathered soils of the group. In a few cases exchangeable K levels were higher in the subsurface than in the surface horizons suggesting that K measurements of the surface horizon may not always give a true indication of the level of plant-available K. Using soil test recommendations for potatoes in Peru published in 1969 (Fitts, 1969), K fertilizer would have been recommended for all but 2 of the 16 Peruvian soils.

Metahalloysite was found in most of the mountain and jungle soils while kaolinite appeared to be present

in the coastal soils; however, the presence of any kaolinite in the jungle and mountain soils would have been masked by the metahalloysite peaks in the X-ray diffraction patterns. Some illite was found in many of the soils, although in about one half of the soils the illite was poorly structured and present in small amounts. If these soils are as young as is believed, the illite could just be forming from primary minerals. In most cases the chlorite and vermiculite present was in interstratified systems. There was a noticeable absence of feldspar in the clay fraction of the 4 northern mountain soils although it may be present in small amounts in the larger fractions, since total soil K levels for the soils varied from 0.15 to 0.86% K.

One soil from the northern mountains which contained predominantly montmorillonite and another soil from the northern mountains did not contain quartz, suggesting that the areas in which these soils are located is not intensively weathered. Allophane was detected in one of the Peruvian soils and was suspected to be present in several others.

To evaluate the susceptibility of interlayer K to exchange and determine how fast it will diffuse from the

clay lattice, soil samples were equilibrated with solutions containing NaTPB for different time periods. After 2000 hr, from 1.9 to 66.9 me K/100 g of K were removed which represented 8.7 and 86.6% of the total K present in the soils. Rates of K release as calculated by the K removed from 10 to 1000 hr, where the rate of K removed appeared to be decreasing at a logarithmic rate, varied from -0.03 to 7.43 me K/100 g/wk demonstrating the wide variability in the ability of these soils to release K. The amounts of K released and the rates of K release were related to the amount and type of clay minerals present in the clay fraction. The soils with low K supplying capacities contained none or very small amounts of illite, and when illite was present, it was poorly structured as indicated by low, broad 10 Å peaks. Larger amounts of more crystalline illite, as indicated by higher, sharper 10 Å peaks, was present in all of the soils which had medium K supplying capabilities. Illite in the soils with high K supplying capabilities was well crystallized and may possibly be muscovite and biotite micas.

The amounts of available K and rates of K release from plant-available forms were determined by growing

five successive oat crops for two weeks each on 100 g soil samples. Amounts of K removed by the 5 oat crops varied from 0.35 to 3.24 me K/100 g soil and rates of K release, as determined by the linear regression slopes of cumulative K uptake from the 2nd to the 5th crop, varied from 0.016 to 0.215 me K/100 g/wk. The amounts of K removed by intensive cropping were not well correlated with K extracted with ammonium acetate ($r = 0.388$); however, if only the uptake data from the first of the five crops were considered, the correlation was higher ($r = 0.693$), and was much higher when only those soils with low potassium supplying capabilities were used for computing the correlation coefficient ($r = 0.979$). This would be expected since a major source of K for plants from these soils would be from exchangeable forms.

In contrast those soils with well crystallized illite released substantial amounts of K during cropping, but had low exchangeable K levels indicating that relatively large amounts of K can diffuse from the clay mineral lattice during cropping.

Total K was extremely variable in the soil as was the total K content of the sand, silt and clay fractions. For those soils from which high amounts of K were removed

with NaTPB and by intensive cropping, there was a higher correlation between K removed and the percent K in the sand than with the percent K in the silt, which further indicates that these soils are relatively unweathered. Total K was much better related with K uptake as the cropping progressed indicating that higher amounts of K were being removed from nonexchangeable sources and that the higher the total soil K, the easier it can be removed.

The concentration of K in solution was not related to K uptake by plants for any of the croppings which suggests that for the soils studied, K capacity factors are much more important than K intensity factors in supplying K to plants. This may be misleading due to the conditions under which the crops were grown, i.e. daily additions of water and a high concentration of roots in a small soil value.

From this study, the following conclusions can be made:

1. The soils in Peru vary in degree of weathering as was indicated by variation in the chemical properties of the soil profile and the clay minerals present.

2. Although there are wide differences in the ability of these soils to release K under stress conditions (NaTPB), variations in K release could frequently be explained by the presence and crystallinity of illite in the clay fraction; using these two criteria the soils could be grouped as having low, medium and high K supplying capabilities.

3. The poor relationship between K extracted with NaTPB for 15 min and K uptake by plants is probably due to different sources of plant available K and the mechanism supplying K to plants.

4. Total K uptake by short-term intensive cropping was not well related to K extracted with ammonium acetate although this relation can be improved by considering uptake from only the first harvest or considering only those soils classified as having low K supplying capacities.

5. Due to differences in mineralogy and K release mechanisms, a single extractant may not be adequate to evaluate the ability of these soils to supply K to plants.

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APPENDIX

Plate 1.--X-ray diffraction patterns of the clay fractions from soils 3 and 4 (northern mountains).

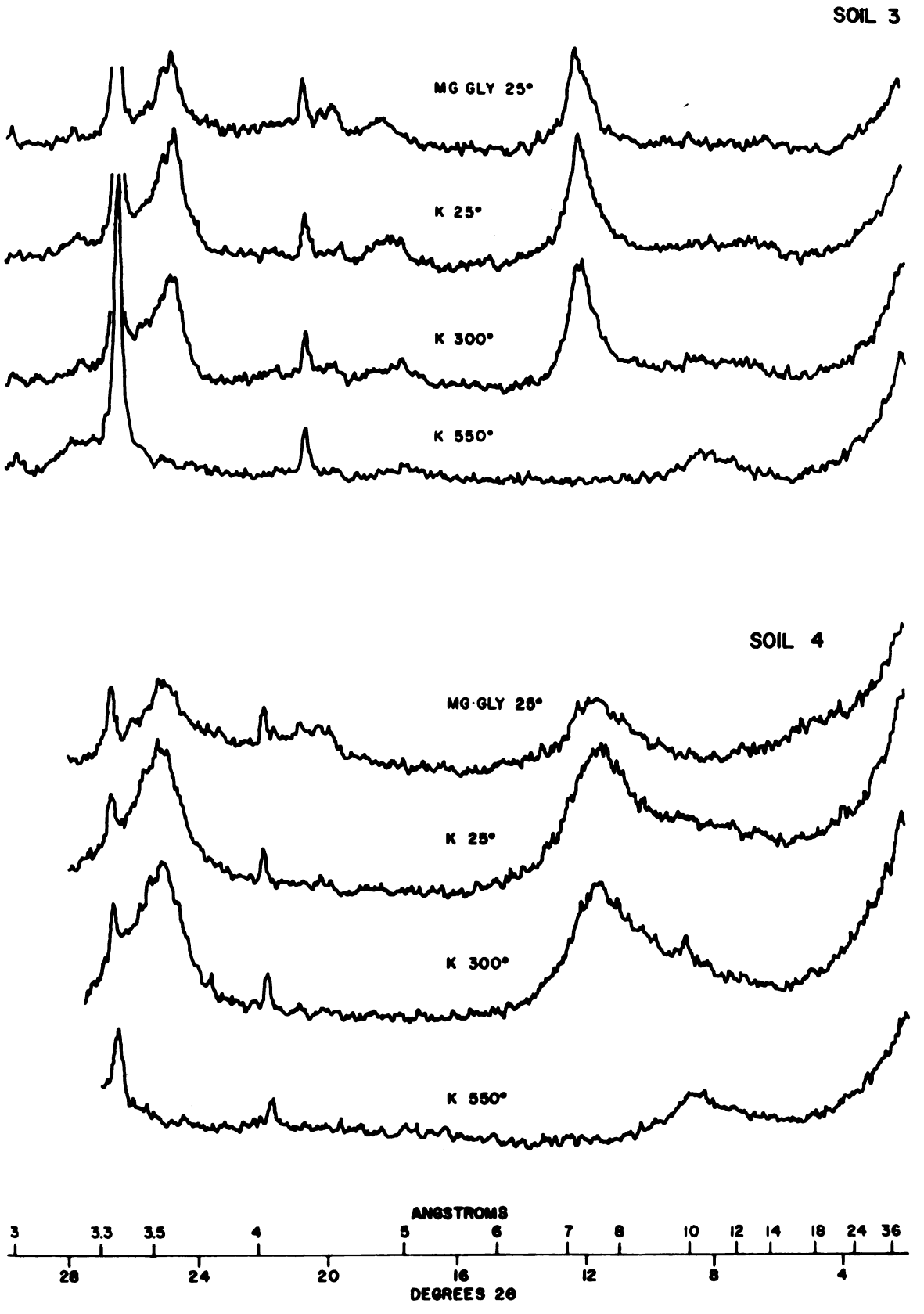

SOIL 3
MG GLY 25°
K 25°
K 300°
K 550°
SOIL 4
MG·GLY 25°
K 25°
K 300°
K 550°
ANGSTROMS
3
3.3
3.5
4
5
6
7
8
10
12
14
18
24
36
28
24
20
16
12
8
4
DEGREES 2θ

Plate 2.--X-ray diffraction patterns of the clay fractions from soils 5 and 6 (northern mountains).

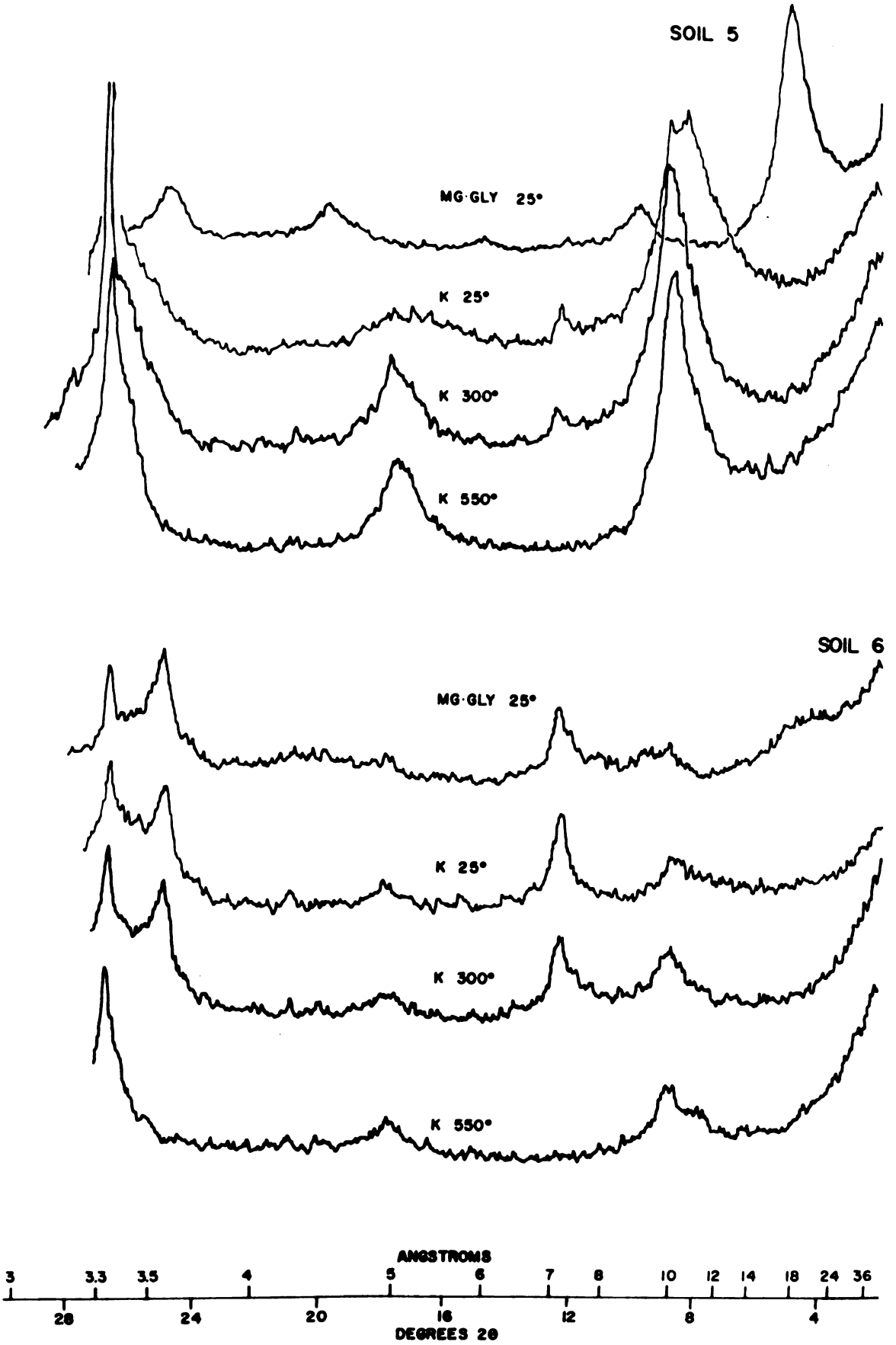

SOIL 5
MG·GLY 25°
K 25°
K 300°
K 550°
SOIL 6
MG·GLY 25°
K 25°
K 300°
K 550°
ANGSTROMS
3
3.3
3.5
4
5
6
7
8
10
12
14
18
24
36
28
24
20
16
12
8
4
DEGREES 2θ

Plate 3.--X-ray diffraction patterns of the clay fractions from soils 8 and 10 (southern mountains.

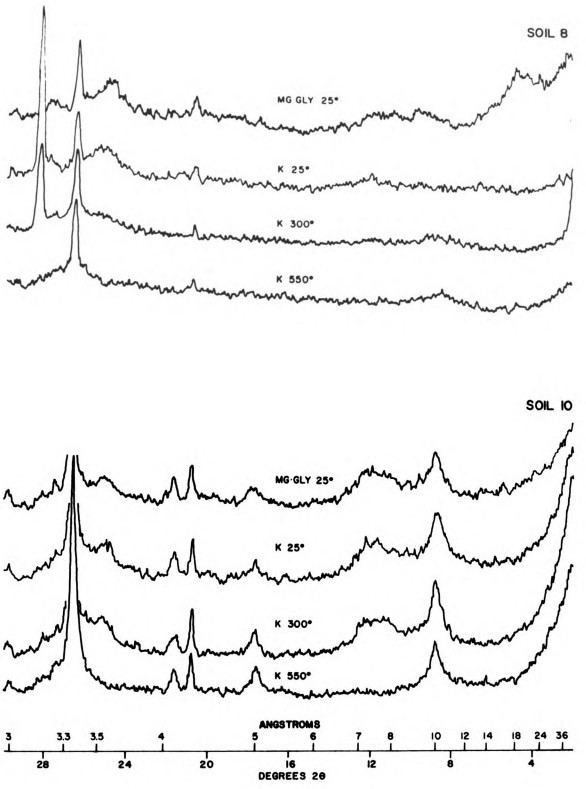

SOIL 8
MG GLY 25°
K 25°
K 300°
K 550°
SOIL 10
MG-GLY 25°
K 25°
K 300°
K 550°
ANGSTROMS
3
3.3
3.5
4
5
6
7
8
10
12
14
18
24
36
28
24
20
16
12
8
4
DEGREES 2θ

Plate 4.--X-ray diffraction patterns of the clay fractions from soils 12 and 14 (southern mountains).

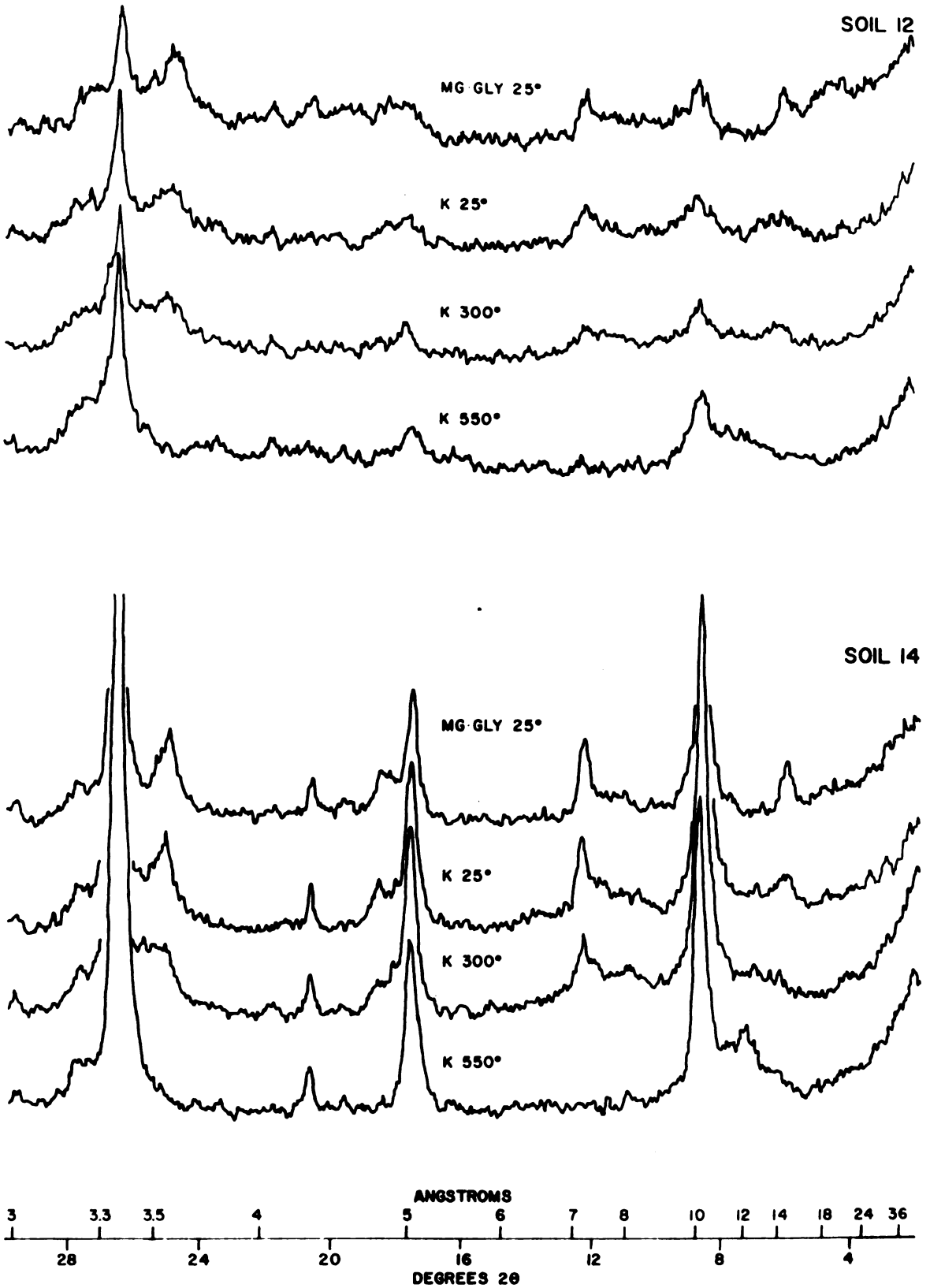

SOIL 12
MG GLY 25°
K 25°
K 300°
K 550°
SOIL 14
MG GLY 25°
K 25°
K 300°
K 550°
ANGSTROMS
3
3.3
3.5
4
5
6
7
8
10
12
14
18
24
36
28
24
20
16
12
8
4
DEGREES 2θ

Plate 5.--X-ray diffraction patterns of the clay fractions from soils 16 and 17 (central mountains).

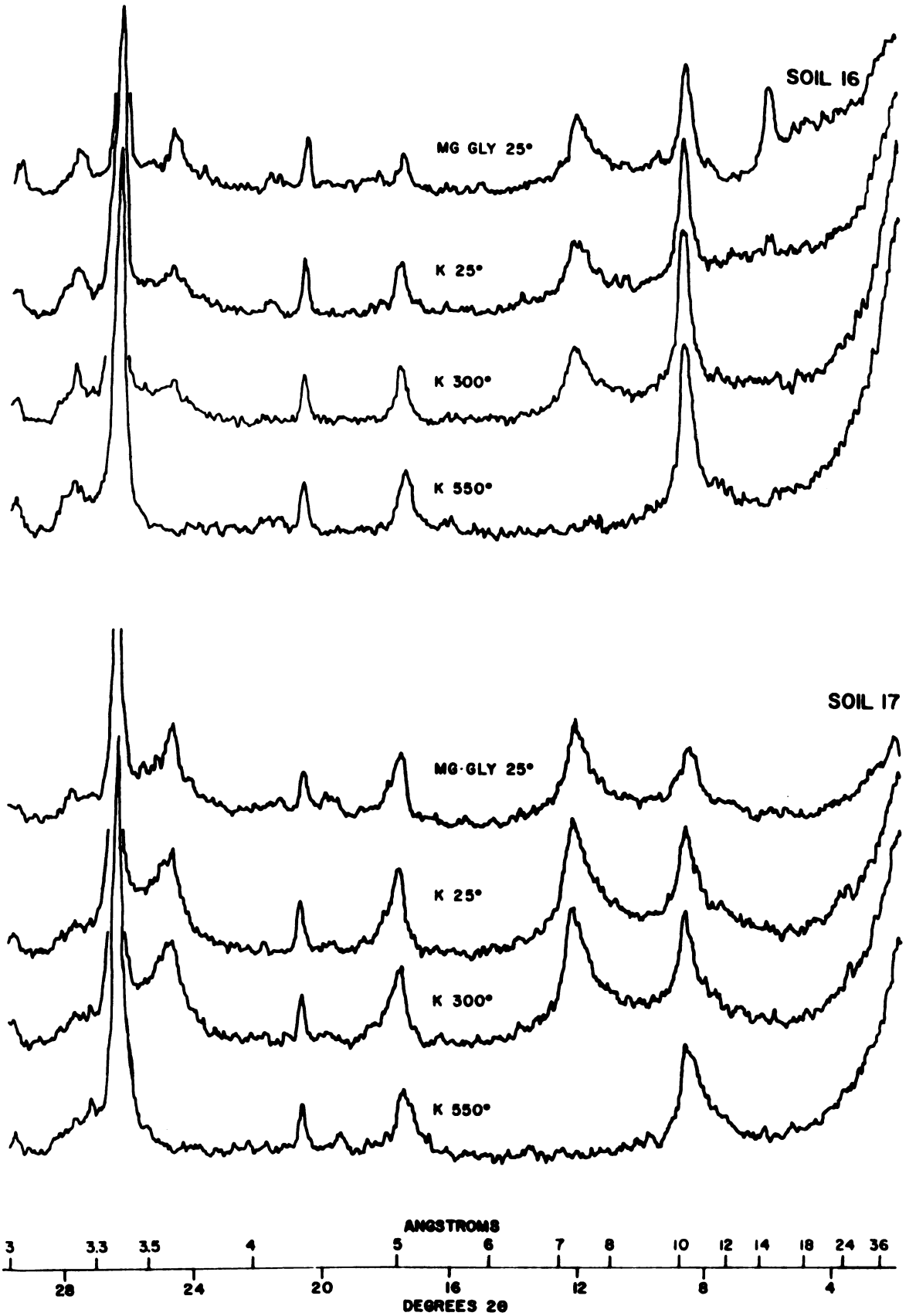

SOIL 16
MG GLY 25°
K 25°
K 300°
K 550°
SOIL 17
MG·GLY 25°
K 25°
K 300°
K 550°
ANGSTROMS
3
3.3
3.5
4
5
6
7
8
10
12
14
18
24
36
28
24
20
16
12
8
4
DEGREES 2θ

Plate 6.--X-ray diffraction patterns of the clay fractions from soils 21 (central mountains) and 24 (central jungle).

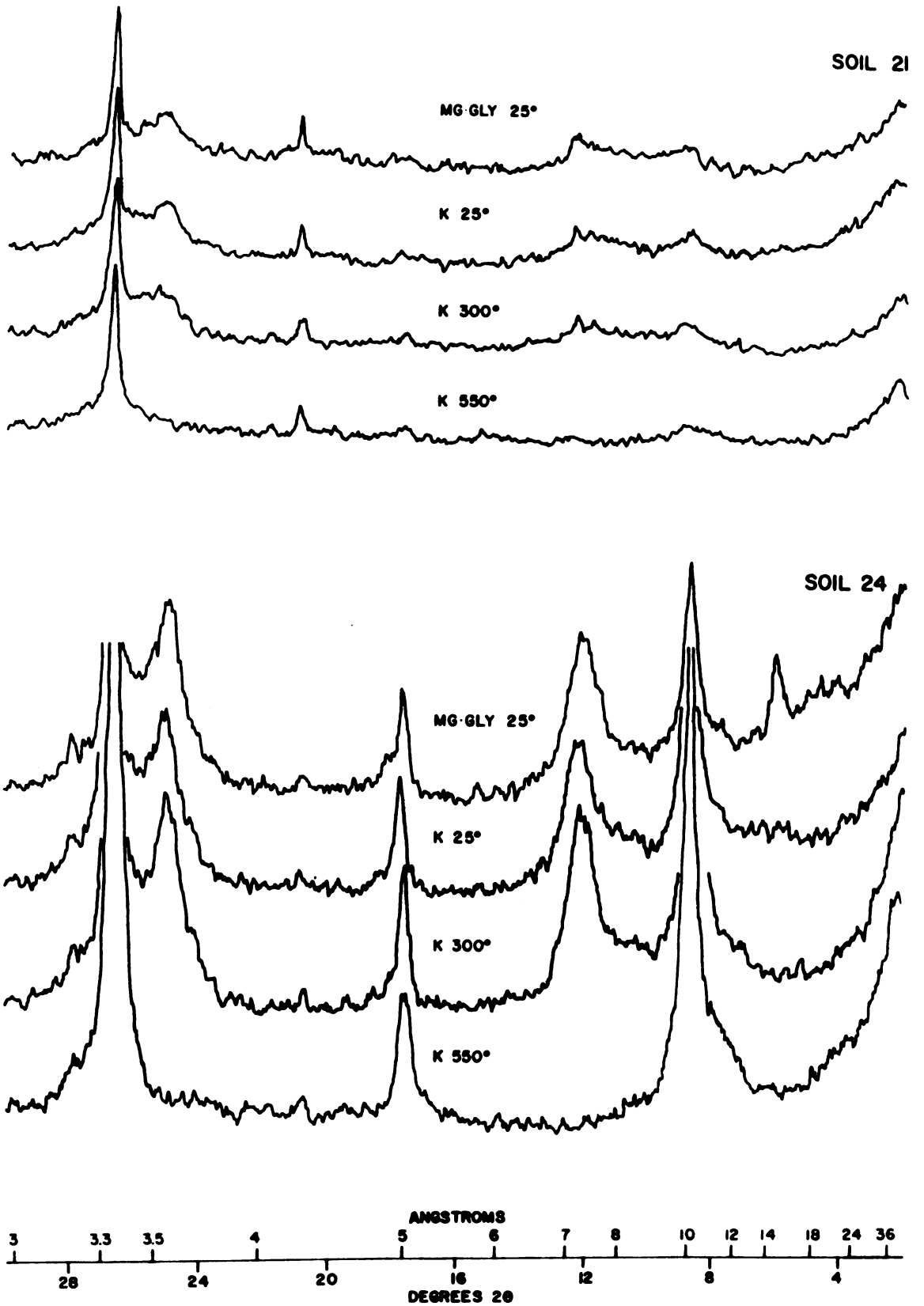

SOIL 21
MG·GLY 25°
K 25°
K 300°
K 550°
SOIL 24
MG·GLY 25°
K 25°
K 300°
K 550°
ANGSTROMS
3
3.3
3.5
4
5
6
7
8
10
12
14
18
24
36
28
24
20
16
12
8
4
DEGREES 2θ

Plate 7.--X-ray diffraction patterns of the clay fractions from soils 26 (central mountain) and 27 (coast).

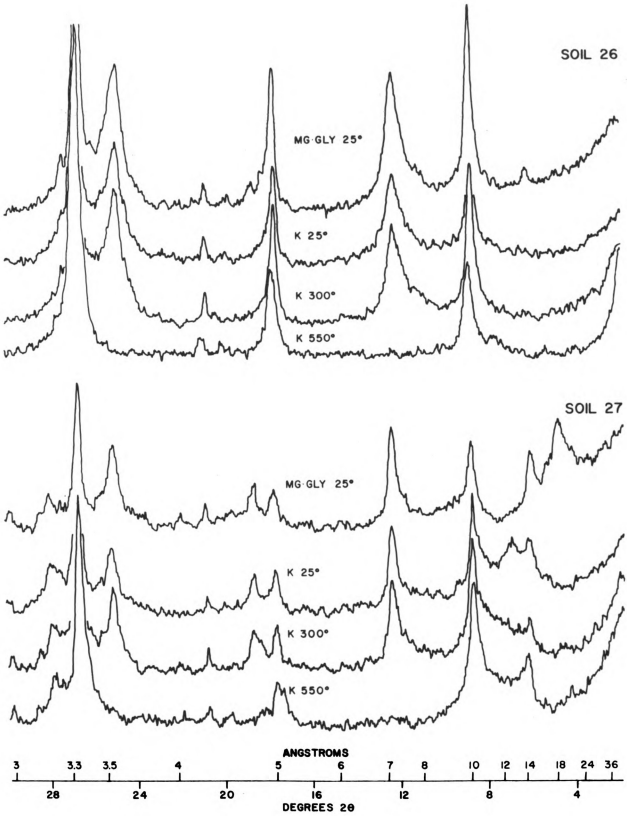

SOIL 26
MG·GLY 25°
K 25°
K 300°
K 550°
SOIL 27
MG·GLY 25°
K 25°
K 300°
K 550°
ANGSTROMS
3
3.3
3.5
4
5
6
7
8
10
12
14
18
24
36
28
24
20
16
12
8
4
DEGREES 2θ

Plate 8.--X-ray diffraction patterns of the clay fractions from soils 28 (coast) and 29 (central jungle).

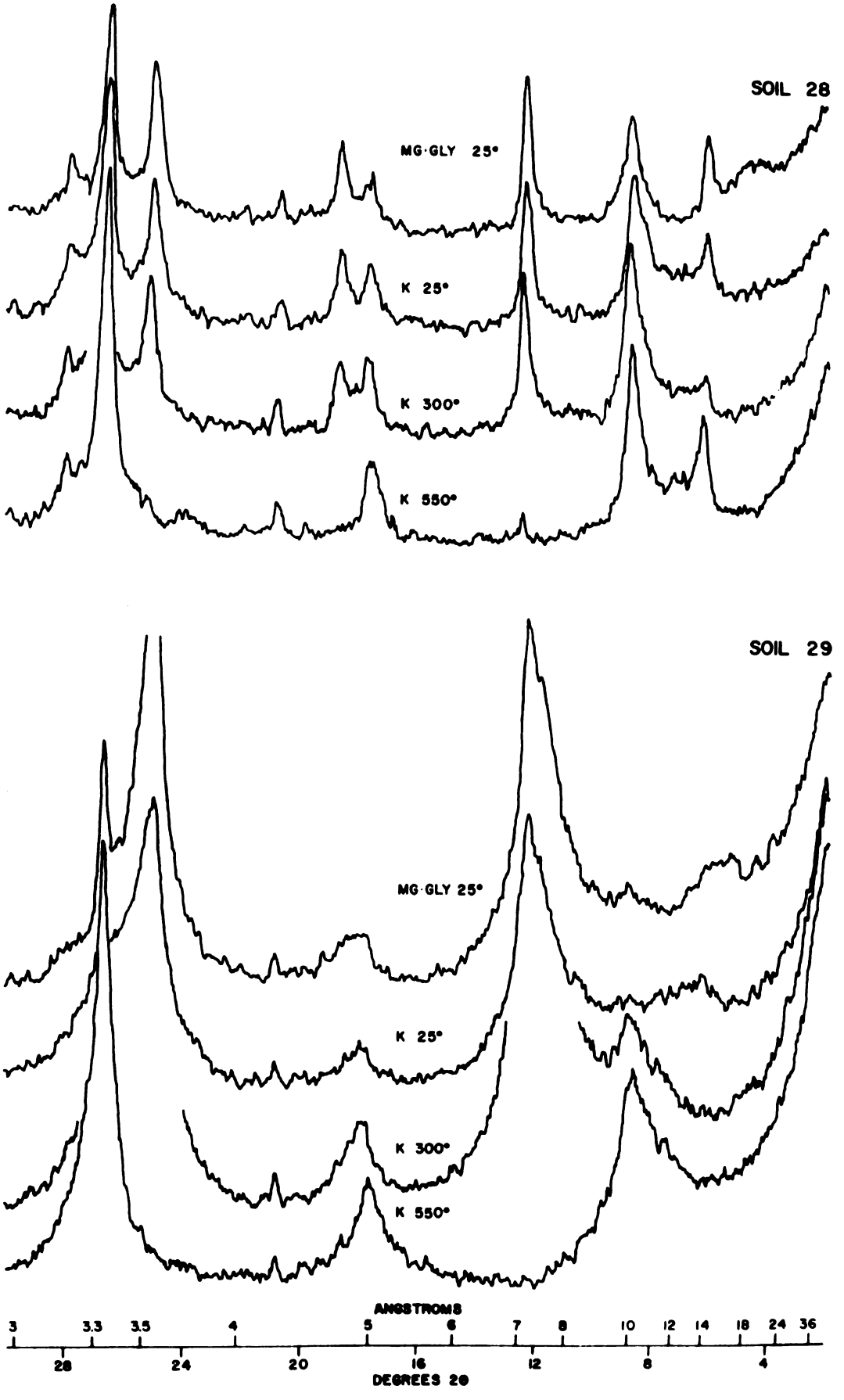
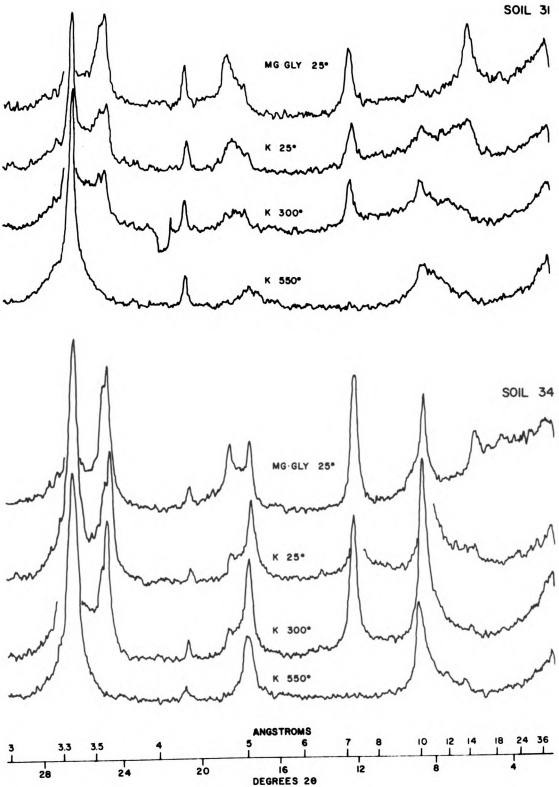

SOIL 28
MG·GLY 25°
K 25°
K 300°
K 550°
SOIL 29
MG·GLY 25°
K 25°
K 300°
K 550°
ANGSTROMS
3
3.3
3.5
4
5
6
7
8
10
12
14
18
24
36
28
24
20
16
12
8
4
DEGREES 2θ

Plate 9.--X-ray diffraction patterns of the clay fractions from soils 31 and 34 (Michigan).


SOIL 31
MG GLY 25°
K 25°
K 300°
K 550°
SOIL 34
MG·GLY 25°
K 25°
K 300°
K 550°
ANGSTROMS
3
3.3
3.5
4
5
6
7
8
10
12
14
18
24
36
28
24
20
16
12
8
4
DEGREES 2θ