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A FRACTIONATION OF ACID-SOLUBLE NON-EXCHANGEABLE POTASSIUM IN SOME NEW ZEALAND SOILS INTO AVAILABLE AND NON-AVAILABLE FORMS

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INTRODUCTION

One of the most ubiquitous of the mineral elements present in plants, potassium plays an important and essential rôle in their nutrition, being required in large amounts for healthy plant growth. Unlike nitrogen, phosphorus, calcium and magnesium, potassium does not enter into permanent organic combinations in plants but appears to exist in solution as potassium ions in conjunction with soluble inorganic and organic anions. Consequently, specific rôles in the growth of plants are difficult to assign to potassium and only by inference from comparisons of normal and potassium deficient plants can functions be attributed to potassium. The following summary of the effects of potassium on the physiology of plants, abstracted from the review made by Lawton & Cook (1955), shows that potassium affects the following processes.

POTASSIUM IN PLANT NUTRITION

1. Synthesis of simple sugars and starch. Low potassium plants tend to have lower carbohydrates than higher potassium plants. Reducing sugars tend to increase compared with the non-reducing sugars, when potassium is low, indicating some rôle in the condensing of hexose sugars. The lower starch and cellulose levels result in thinner and weaker cell walls and stems.
2. Nitrate absorption. Nightingale (1943) and others have suggested that the uptake of nitrate ions by plants is accelerated by the presence of potassium.
3. Nitrate reduction and protein synthesis. From comparisons of potassium deficient and normal plants, soluble organic nitrogen fractions, e.g. amino and amide forms were higher in the potassium deficient plants. Together with an initial accumulation of carbohydrates in the early stages of potassium deficiency, this is taken to indicate that potassium is essential to protein synthesis.
4. Cell division. Because of the concentration of potassium always found in actively growing tissues, even at the expense of potassium removal from older tissues, it has been concluded that potassium must have some function, probably one associated with protein synthesis, in cell division.

Other functions in which potassium is thought to play some rôle, are in the formation of organic acids and oils, in the resistance to disease, in the maintenance of turgor and in photosynthesis.

If available in very large amounts, luxury consumption of potassium occurs, sometimes to the extent of inducing deficiencies of magnesium on low magnesium soils (Russell, 1950).

Under conditions of low available potassium, deficiency symptoms become apparent. Depending on the type of plant, these deficiency symptoms take various forms, usually as manifestations of damaged or malformed tissue. Symptoms usually appear first in the older tissues because of the translocation of potassium to the actively growing tissues. Some symptoms of potassium deficiency are as follows (Table 1).

TABLE 1

POTASSIUM DEFICIENCY SYMPTOMS IN PLANTS

Plant	Symptoms
Grasses and small grains.	Stunted thin growth with excessive tillering. Edge scorch with yellowish older leaves.
Corn.	Stunted growth, yellowing tips and margins of older leaves. Poorly filled cobs.
Clovers and Lucerne.	Small white spots on leaves, followed by general yellowing of leaves.
Brassica Crops.	Bluish green leaves with slight chlorosis. Leaf margins show scorching.
Potatoes.	Stunted dull bluish green growth. Very reduced yields of poor quality.
Tomatoes.	Similar to potatoes, with slight chlorosis with brown marginal scorching. Fruits ripen unevenly with greenish-yellow patches persisting.

References - Wallace, Mineral Deficiencies in Plants, pp 58-9
Lawton and Cook (1954).

Although in New Zealand, potassium deficiencies and responses are not widespread, considerable areas do occur where responses are found to potassic fertilizers. Figure 1 shows the areas of New Zealand where potassium responses have been recorded. As farming becomes more intensive and as areas become farmed for longer periods, more potassium deficient areas are being observed. The two forms of potassium deficiency seen most frequently are poor clover growth with associated nitrogen deficiency, giving characteristic patchy light yellowish green pastures and unthrifty lucerne with yellowish spotted leaves.

AVAILABLE POTASSIUM

Although most soils contain from 1-2% of potassium, only a small fraction of this, usually from 1-2% is available to plants. The available potassium is regarded as that potassium which is capable of being taken up by plants and used for their growth. The soil potassium is not equally available to plants, the availability of some forms being so low that they are virtually unavailable to plants. The available fraction includes the water soluble and exchangeable potassium, which are readily available to plants, together with some more tightly held potassium, the whole being in equilibrium with the remaining 98-99% of the total soil potassium, which is present as unweathered and partially weathered minerals.

The availability of the potassium in any particular soil will depend on the rate at which the equilibria are set up and on the ability of the plant to take up potassium from the soil. Estimations of the total potassium available to plants will therefore depend on these reaction rates and on the type of plant used.

Because of the effect of potassium on crop quality and quantity, it is necessary to be able to forecast the onset of potassium deficiency conditions. An examination of the relevant literature will show that although many techniques have been recommended, including mineralogical determinations, total potassium determinations, exchangeable potassium determinations, intensive plant growth over short and long periods of time, electrodialysis and strong acid extractions, as yet, no entirely satisfactory technique has been evolved and that further study to elucidate and eliminate the causes of inaccuracies and variations in published methods, is warranted. Any technique to be satisfactory must be accurate without being too laborious and must be reasonably rapid.

FORMS OF POTASSIUM IN SOILS

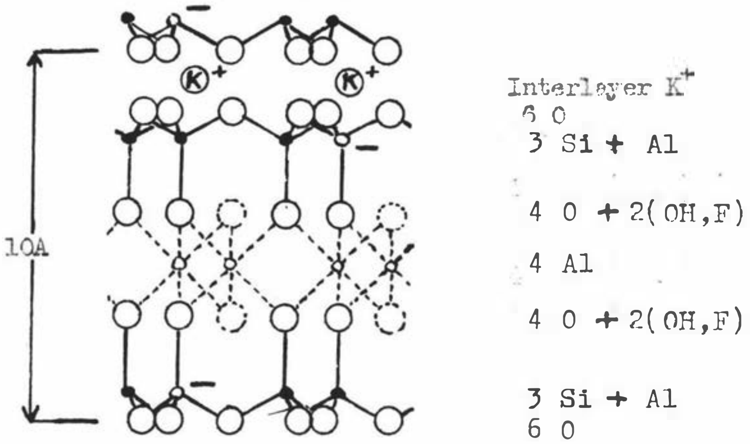
Potassium occurs in soils in several forms, the simplest of which, is the free potassium cation, K^+, the form in which the water soluble potassium occurs, this form being in equilibrium with the colloidally bound exchangeable potassium. Because of the ease with which these two forms interchange, they are usually grouped together and in this study, this practice is carried out unless otherwise stated. In distinction to its simpler forms where it is associated with a charged surface, in its more complex forms, potassium is associated with definite atomic structures of the unweathered and partially weathered minerals. Depending on the ease of breakdown of these structures on weathering, the potassium changes to the simpler ionic form.

Included in the unweathered and partially weathered minerals which contain potassium, are many which contain small amounts of potassium as an impurity. There are, however, a few minerals which contain large amounts of potassium, including micas, some felspars, glauconite and leucite.

The potassium containing micas, which are silicate minerals with structures of sheets of silica and alumina, include

a. **Muscovite.** $KAl_2(AlSi_3)\,O_{10}(OH,F)_2$, white mica, a primary mineral with a layer lattice structure of 2 sheets of silica tetrahedra, each sharing 3 oxygen atoms to form an infinite 2 dimensional sheet, joined by a sheet of alumina octahedra where one third of the oxygen atoms are replaced by hydroxyl and fluoride, these oxygens, hydroxyls and fluoride being shared with the silica tetrahedra. One quarter of the silcon in the tetrahedral layers is replaced by aluminium leaving a nett negative tetrahedral charge which is balanced in muscovite by interlayer potassium ions, which share their charges between adjacent layers, binding them together closely. The bond is strong enough to prevent the entry of water molecules between layers and the basal spacing of 10 A is too small to permit free entry of cations between the layers. The mineral is therefore non-expanding. The atomic structure of muscovite is shown in diagram form in Figure 2.

FIGURE 2



Schematic Representation of the Structure of Muscovite

b. **Sericite,** a secondary mica, of composition and structure similar to muscovite, but normally occurring in fine scales.
c. **Biotite,** $K(Mg,Fe)_3\ (AlSi_3)\ O_{10}(OH,F)_2$, brown mica, iron replaces magnesium to a variable extent. The structure is similar to that of muscovite but the alumina octahedral sheet is replaced by a magnesium-iron oxygen-hydroxyl-fluoride sheet.
d. **Biotite-hydrous biotite-vermiculite series,** a structure similar to biotite, with variable potassium and hydroxyl content and with extensive replacement of iron by magnesium in vermiculite.
e. **Illite,** a non-expanding clay with a structure similar to unweathered micas with a basal spacing of 10 A, but with increased hydroxyl and lower potassium. Some other products of micaceous weathering are similar to illite but have expanding lattices. These include clay-vermiculite. (Fieldes and Swindale, 1954).

The other main class of potassium containing minerals is the felspars which differ from the micas in that instead of the layer lattice sheet structure of the micas, they possess framework structures where the unit tetrahedra are linked by all four corners to make 3 dimensional frameworks of composition $n(Si,Al\ O_2)$. The negative charge arising from the substitution of aluminium for silicon is balanced by cations fitting into spaces in the framework. Because the cations are present only to balance the negative charges in the framework, continuous series of felspars differing in the content of alkali and alkali earth metals are found. Thus most felspars contain potassium as an impurity and the potassium felspars do not contain as much potassium as would be expected from the theoretical type formula. The following felspars, however, contain potassium as a major alkali element.
a. **Orthoclase,** $KAlSi_3O_8$, a monoclinic felspar.
b. **Microcline,** $KAlSi_3O_8$, a triclinic felspar.
c. **Soda orthoclase** and **anorthoclase,** where sodium replaces part of the potassium of orthoclase and microcline.

The other soil forming potassium containing minerals, which are much rarer than either the micas or felspars, are **glauconite,** essentially a hydrous silicate of iron and potassium with some aluminium, magnesium and calcium present, and leucite, $KAlSi_2O_6$, a component of basic volcanic rocks low in silica. Neither is a common component of New Zealand rocks, although glauconite is a component of greensands which occur in scattered areas in Hawke's Bay, Canterbury and Marlborough.

The equilibria between the forms of soil potassium may be represented thus

Native, unweathered mineral potassium, 90 - 98% of total soil potassium, includes the micas, muscovite, sericite, biotite and vermiculite, and the felspars, orthoclase, microcline, and glauconite and leucite.

↓ Loss of potassium to ionic form

Partially weathered minerals containing less potassium, including hydrous micas, illite, and various intermediates.

⇅

Moderately available potassium but not exchangeable.

⇅

Exchangeable potassium
⇅
Water soluble potassium
} Potassium present as cation, K^+.

The rate of release of potassium from the mineral forms to the available forms depends on the stability of the minerals concerned, upon their potassium content and on the intensity of weathering.

WEATHERING OF POTASSIUM MINERALS

The stability of the various minerals depends to a considerable extent on their particle size and somewhat different orders of stability are found for coarse particles and for fine particles.

For the coarse grained particles, sand and coarse silt, the susceptibility to weathering is of greater importance in governing the rate of weathering than variations in specific surface, and there is general agreement between different stability series. The branched stability series for coarse grained minerals, presented by Goldich (1938) viz.

Mafic		Felspathic		
olivine		calcic	plagioclase	Increasing ↓
augite				
hornblende		to		
biotite		alkalic		
	potassium felspar			Stability
	muscovite			
	quartz			

is similar to the weathering sequence proposed by Graham (1950). It differs from that of Marel (1953) for magmatic minerals subjected to tropical weathering, which, in order of increasing stability and with the non-potassium heavy minerals omitted, is

basic volcanic glass, biotite, anorthite....oligoclase, muscovite, orthoclase, microcline, albite, quartz.

For the finer grained particles $< 5\mu$, fine silt and clay, the weathering sequence is somewhat different and is influenced markedly by the specific surface. The sequence of Jackson et al (1952) is as follows:
1. Gypsum, 2. Calcite, 3. Olivine-hornblende, 4. Biotite, 5. Albite,
6. Quartz, 7. Muscovite, 8. Interstratified 2:1 layer silicates and vermiculite,
9. Montmorillonite, 10. Kaolinite, 11. Gibbsite, 12. Haematite, 13. Anatase.

Glauconite and Magnesium chlorite are included in Stage 4.
Microcline and orthoclase " " " " 5.
10 A sericite and illite " " " " 7.
Partially expanded hydrous micas " " " " 8.
Vermiculite with distinct 14 A spacing " " " 8.5

Jackson states that normally only 3 to 5 minerals are present in the colloidal fraction of any one soil horizon, with one or two minerals dominant.

Fieldes and Swindale (1954), on the basis of examination of the mineral colloids of New Zealand and some Pacific Island soils, proposed a weathering sequence which differed from that of Jackson et al (1952) in that muscovite is grouped with biotite and that volcanic glasses are included in the sequence. They presented a flow sheet, reproduced here in Figure 3, illustrating their weathering sequence and showing the relationship of the secondary minerals to the primary minerals and to one another.

FIGURE 3

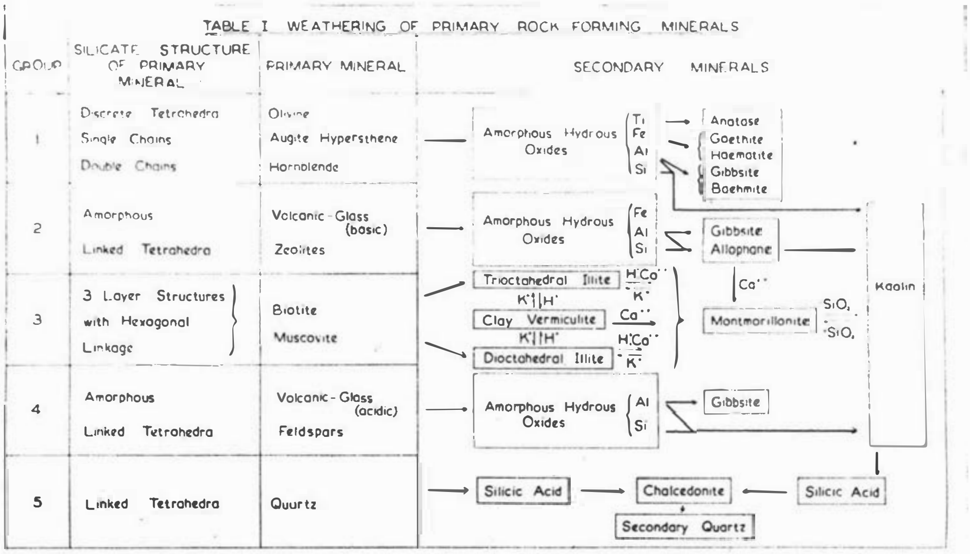


TABLE I WEATHERING OF PRIMARY ROCK FORMING MINERALS

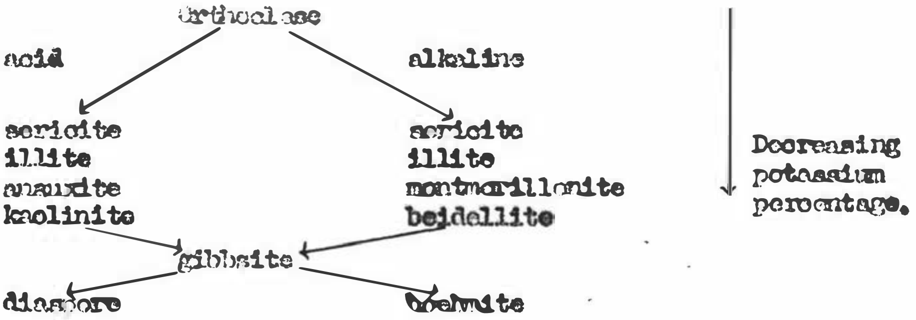
GROUP	SILICATE STRUCTURE OF PRIMARY MINERAL	PRIMARY MINERAL
1	Discrete Tetrahedra Single Chains Double Chains	Olivine Augite Hypersthene Hornblende
2	Amorphous Linked Tetrahedra	Volcanic-Glass (basic) Zeolites
3	3 Layer Structures with Hexagonal Linkage	Biotite Muscovite
4	Amorphous Linked Tetrahedra	Volcanic-Glass (acidic) Feldspars
5	Linked Tetrahedra	Quartz

According to Fieldes and Swindale (1954).

Under normal weathering conditions, monotype minerals are not usually formed. Instead mixed layer clay minerals are formed, these having properties intermediate between those of the simple secondary minerals.

The more resistant minerals tend to persist in greater quantities in the finer fractions and for each mineral there is a minimum size which depends on the intensity and duration of weathering.

The course of weathering of potassic minerals, according to Jackson and Sherman (1955) is as follows.
For felspars in acid and in alkaline environments,



It may be noted that micas and interstratified micas are formed by the weathering of felspars. As the weathering proceeds, potassium is lost from the minerals until the potassium-free minerals, anauxite and montmorillonite, are formed.

The micas, muscovite and sericite (a secondary form of muscovite), weather similarly, as shown above for sericite, as do the mica intermediates of the hydrous mica type. Biotite tends to weather by depotassication and hydration through interstratified biotite-vermiculites and biotite-chlorites to vermiculite, chlorite and montmorillonites. The weathering of vermiculites, chlorites and biotites and their interstratified intermediates has been shown by X-ray diffraction measurements to be reversible. Barshad (1948) showed that a slow exchange of magnesium for potassium of biotite results in a basal spacing of 14 A and that the reaction is reversible. Jackson et al (1952) proposed that, in distinction to the "frayed edge" type of weathering, the removal of potassium in a partially weathered plane proceeded preferentially to the initiation of weathering in an unweathered plane, thus producing interstratified layer silicates, with the properties of both the unweathered unexpanded mineral and the fully expanded, weathered mineral. The principal changes accompanying the chemical weathering of mica, are

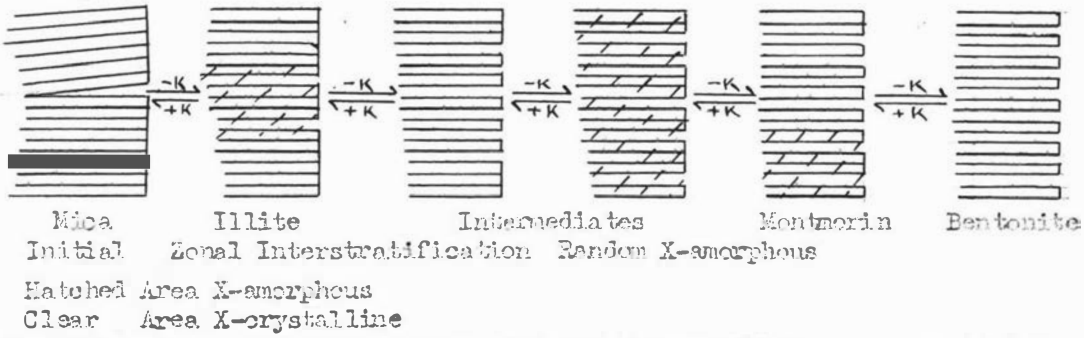
1. A decrease in the basal diffraction intensity and a broadening of the angle of basal diffraction, indicating a less ordered structure.
2. The appearance of basal spacing intermediate between 10 A and 18 A.
3. An increase in the internal surface as measured by $R(OH)_n$ sorption.
4. Lower potassium percentage than theoretical.
5. Higher H_2O percentage or hydroxyl percentage than theoretical.
6. Lower cation exchange capacity than expected from theoretical mica layer charges vacated by potassium replacement.
7. The existence of "slow" exchange, particularly with hot Mg^{++} solutions or in the presence of potassium precipitants and correlated uptake of potassium by partially weathered minerals i.e. potassium fixation.

The sequence of reversible reactions

mica $\rightleftharpoons$ illite $\rightleftharpoons$ "intermediates" $\rightleftharpoons$ vermiculite $\rightleftharpoons$ montmorin $\rightleftharpoons$ Bentonite

was illustrated thus with "intermediates" and vermiculite not distinguished.

FIGURE 4



Under this scheme, illite is a mica with mixed expanded spacings, which may by the further removal of potassium change to vermiculite or montmorins or by fixing potassium, may change into a mica. It may be noted that K^+ in solution converts vermiculite into mica by "slow" exchange. Potassium "fixation" widely reported in soils as a result of drying, may be explained as a function of the reverse-weathering entry of potassium between layers having a high exchange charge.

The weathering of both felspars and micas is accompanied by a release of potassium to the ionic form, the amount and rate of the release of K to available forms depending on the amount of the potassium bearing mineral, its particle size and its stability under the weathering conditions prevailing.

For example, under the tropical conditions of Indonesia, sandy soils derived from biotite containing rocks, show no potassium responses unless they are so strongly weathered that all the biotite has disappeared. In the clayey lowland soils, the plagioclases, oligoclase, andesine and anorthite, and amphiboles, which are all very readily weathered under tropical conditions, are able to supply from the traces of potassium present as impurities, sufficient potassium for normal crop growth (Marel, 1947).

Under temperate conditions, the relationship between potassium response and the relative abundance of potassium containing minerals is not so clearly defined. Higher than average potassium availability with low potassium responses, was associated with high 10 A mica in the fine clay (Rouse and Bertramson, 1950) and high microcline in the silt (Phillippe and White, 1952) of Indiana soils, with high potassium felspar content of Belgian polder soils (de Leenheer, 1950) and with abundant glauconite in soils derived from greensands (Reitemeier, 1951).

METHODS OF ESTIMATING AVAILABLE POTASSIUM

It is apparent that although a study of the weathering processes shows the way in which potassium is released, it does not provide a measure of the availability of the soil potassium. It is necessary to resort to other methods which will integrate the availabilities of the different forms into a parameter which represents the availability of potassium in the soil as a whole.

The majority of the methods published for the estimation of the available potassium are not entirely satisfactory for the following reasons.

Mineralogical Determinations. These have not proved to be a satisfactory basis for forecasting the potassium status of a soil except in the few cases quoted on page 9. If done on the clay and silt fractions, they require elaborate equipment. It is probable that as further knowledge of the clay and silt minerals accumulates, more use will be made of this method. Optical methods, which are restricted to the sands and coarse silt fractions, must be inaccurate because they overlook the most reactive portion of the soil, the clay and finer silts.

Total potassium determinations are of little value in themselves as they give no indication of the availability of the potassium present.

Exchangeable potassium values have not been found to be a reliable guide to the amount of potassium available to plants over a long period, although they give a reasonable indication of the amount of potassium immediately available to plants, as shown by the potassium percentage in the plant tissue. Seay, Attoe and Truog (1949) found that the potassium percentage in alfalfa was related to the exchangeable potassium in moist soil samples, with exchangeable potassium ranging from 0.1me % to 0.6me % by the equation.

%K in crop = 1.81 log lb.exch.K / acre - 2.84

Correlation Coefficient r = 0.81.

Similar relationships were found for tobacco and oats by Attoe (1946, 1949).

If the range of soils is narrow, fair correlations with potassium availability may be found but little or no correlation exists between exchangeable potassium and available potassium when a wide range of soils is considered.

Plant growth may be either over a short period as for the Neubauer test or over long periods. Short term growth gives very little better indication of potassium availability than exchangeable potassium values and long term testing is of little practical use in giving an immediate indication of a deficiency and is too laborious to be a routine test, although it is by definition, the reference method for determining long term availability of soil potassium to plants.

Because of variations in cropping procedures, it is not possible to compare directly potassium availability data. Variations, not related to the potassium content, in the physical condition of the soils cropped e.g. in the structure, aeration, water holding capacity and drainage, and in the

TABLE 2.

SUMMARY OF SOME PUBLISHED RESULTS OF POTASSIUM UPTAKE BY PLANTS

	Number of soils	Total K in crop me/100gm. soil	Non-exch. K in crop me/100gm. soil	Nature of crop	Cropping period Months	Reference
Hawaii	12	0.45 - 3.0	0.4 - 1.5	7 grass crops	42	Ayers (1949).
New Jersey	20	0.02 - 0.5	0.0 - 0.3	7 alfalfa	12	Bear, Prince and Malcolm (1944).
New York	11	0.03 - 0.58	0.0 - 0.45	5 ladino clover	11	Chandler, Peech and Chang (1945).
Wisconsin	6	0.10 - 0.25	0.0 - 0.15	4 oat crops	9	Evans and Attoe (1948).
Mississippi and Alabama	8 5	0.27 - 1.15	0.2 - 0.75	8 cuts millet	18	Gholson and Hoover (1949).
5 States	14	Not quoted	0.1 - 0.9	15 ladino clover	24	Reitemeier et al (1948).
Alabama	10	0.15 - 0.25	0.0 - 0.15	12 crops	60	Stewart and Volk (1946).
Iowa	15	0.15 - 1.05	0.1 - 0.45	9 cuts alfalfa	10	Pratt (1951).
Ohio	18	0.15 - 0.75	0.20- 0.65	5 corn crops	10	Schmitz and Pratt (1953).

nutrient availability status of the soils will all influence the volume of crop growth.

Table 2 summarizes some of the results published.

It may be seen from Table 2 that for most soils, potassium other than exchangeable potassium was available to the crops used.

Some of the variation between results is probably due to variations in the type of plants used. Differences in the ability to use soil potassium have been noted by several workers. Drake and Scarseth (1939) found that 12 crop plants differed markedly in their ability to remove potassium from soils of low available supply. Lewis and Eisenmenger (1948) showed that the more primitive plants such as larkspur were more efficient feeders on nonexchangeable potassium in the form of ground orthoclase than the more highly developed plants such as lettuce and spinach. Mattson (1948) suggested that the uptake of cations by different plant species might be partially controlled by the cation exchange capacity of the colloidal fraction of the plant roots. Gray, Drake and Colby (1953) observed that plants with fine roots of low cation exchange capacity per given area of surface, such as bentgrass and Kentucky bluegrass, are more efficient at taking up available potassium than the coarse rooted plants such as smooth brome grass and ladino clover. However, variations from this cause would be in magnitude not in kind.

In the Neubauer test, in which Rosen rye seedlings are grown for 17 days under standard environmental conditions and the potassium uptake measured by extracting the potassium from the crop, exchangeable potassium usually supplies the bulk of the potassium taken up. In many cases, however, a considerable uptake of nonexchangeable potassium has been reported when allowance is made for the exchangeable potassium remaining in the soil at the end of the test. Because of the short cropping period the uptake of nonexchangeable potassium (if any) found by this method may fail to be a measure of the real availability of the nonexchangeable potassium. ✓ [illegible]

Typical of these reports is the work of Lilleland (ref. in Williams and Jenny (1952)), who found for Californian soils that nonexchangeable potassium was used by the rye seedlings in over two thirds of the 300 samples with initial exchangeable potassium less than 0.4me%.

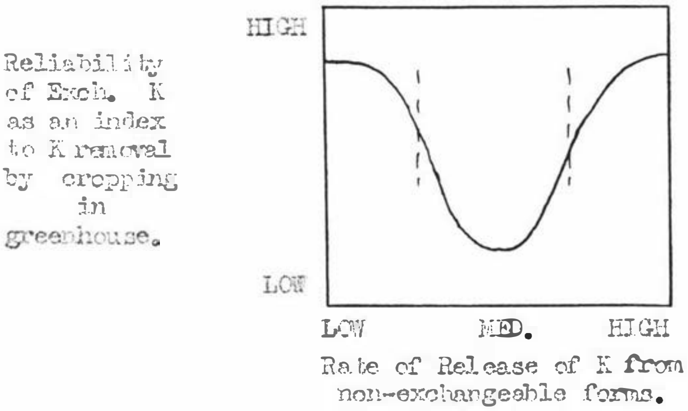
When the amount of soil used for the test was reduced from 100 gms. to 25 gms. by Schachtschabel (1939) the uptake per 100 gms. soil increased for soils of high supplying power, but was unaltered for soils of low supplying power. ✓ Imp.

↓ Ref missing

Similar increases in uptake of nonexchangeable potassium were found by Reitemeier, Holmes and Brown (1950) when they reduced the weight from 100 gms. to 25 gms. of soils from the Northern Great Plains, the increases being from 0.2 me% to 1.3 me%, (the percentage increase being 84%). Although the larger value reported is probably an extreme case and some of the release probably occurred in the air drying of the samples after cropping, it is apparent that potassium other than exchangeable potassium is readily available to plants. Where the residual exchangeable potassium remaining after the termination of cropping is allowed for, release of potassium is found, except with soils of very low potassium supplying power such as the highly weathered, strongly leached Alabama soils studied by Pearson (1952).

The importance to plants of the various forms of soil potassium is expressed by the correlation between those forms and the potassium uptake by plants. Significant correlations between the initial exchangeable potassium and total plant potassium were found by Pearson (1952) where there was a negligible release of nonexchangeable potassium, and by Schmitz and Pratt (1953) for Ohio soils where there was a very considerable release of nonexchangeable potassium. With Tennessee soils, Long and Seats (1953) found there was no relationship between the potassium extracted by 22% $NaClO_4$ in 0.1 N $HClO_4$ and crop yield and that a quick test using this extractant was definitely unsatisfactory. Schmitz and Pratt regard the initial exchangeable potassium level as being of use in forecasting potassium uptake only when the rate of supply of nonexchangeable potassium is very low or very high. At intermediate rates of supply, it is of doubtful value. They depicted their conclusions in figure 5.

FIGURE 5.



(After Schmitz and Pratt, 1953).

Residual Exchangeable Potassium. Peech (1948) states that under cropping, the level of exchangeable potassium falls to a constant level, characteristic of the soil and governed by the rate of release of potassium from nonexchangeable sources and that this level gives a good indication of the potassium supplying power of the soil.

Breland, Bertramson and Borland (1950) observed that although there was no correlation at the 0.05 (P) level between the exchangeable potassium originally present in 23 Indiana soils and the amount released to 8 cuttings of ladino clover in 493 days, after 3 cuttings of clover the exchangeable potassium level was rather closely correlated ($r = 0.67$) with the total potassium released. The correlation coefficient increased to 0.83 by the 8th cutting and for the average of the exchangeable potassium after cuttings, 3, 4, 6 and 8, it was 0.92.

The release of potassium from the various texture separates has shown that, generally, more potassium is released from the finer particles than from the coarser particles. Olsen and Shaw (1943) carried out Neubauer tests on exchangeable potassium-freed 2-10, 10-20 and 20-50 μ silt and fine sand fractions of Clemont, Wooster and Brookston soils. Significant amounts of potassium were taken up from all fractions with the greatest amounts from the finest particles. Merwin (1950) found with sand, silt and clay fractions from 4 New York soils, that the contributions to the total release on storage, were

sand 0-13%, silt 15-51% and clay 40-83%.

No correlation was observed between the release of potassium by the sand and silt fractions and their content of potassium-bearing minerals.

POTASSIUM RELEASE AND FIXATION ON STORAGE AND ON DRYING

The observed release of non-exchangeable potassium on storage was the basis for a laboratory test for estimating the available potassium in soils proposed by Bray and DeTurk (1939) who considered that the level of exchangeable potassium after 6 months storage with the prior removal of exchangeable potassium, was a good index of the potassium supplying power of the soil. They also noted that drying at 200°C brought about the release of potassium when the exchangeable potassium was low and attributed the effect of heat to an increase in the release reaction rate.

Kolterman and Truog (1953) investigating the increase in exchangeable potassium which occurred when the temperature of drying exceeded 110°C, found that where ammonium saturated soils were heated, a rapid increase in exchangeable potassium occurred at about 350°C, the temperature of the exothermic peak for ammonium saturated montmorillonite and vermiculite, where all the ammonium is given up as ammonia. The maximum release of exchangeable potassium occurred at 500°C. Subsequent heatings of the exchangeable potassium freed soils released lesser amounts of potassium, related one to the other by the relationship

$Y = -10 \log X + C$ where Y is treatment number,
and X is amount of K released.

The total potassium released is given by

$\sum_{1}^{Y} X = a(1-r^{Y}) / (1-r)$ where a = 1st extraction less exchangeable potassium.
and r = constant ration $10^{-0.1}$.

From this equation, the total potassium releasable is given by

$\sum_{1}^{\infty} X = 4.85\ a.$

Kolterman and Truog claim that this gives a good indication of the potassium supplying power of soils.

The drying of cropped soils with <0.2 me% exchangeable K compared with 0.2 to 0.5me% exchangeable K in the corresponding virgin soils, was found to produce increases in the exchangeable potassium content of 6 Wisconsin soils over that found for the moist soil samples, the increases varying from 4% for the Plainfield sand to 90% for the Miami silt loam (Attoe 1946). However, when these soils were fertilised with 900 lb. K per acre as KCl (1.15 me%) and stored moist for two months, in all cases, drying after storage *fixed potassium in a non-exchangeable form in addition to any fixed during moist storage. The fixation on drying was apparently independent of that occurring during moist storage. It was independent of liming and the potassium fixed was relatively insoluble in cold 0.5 N HCl in 1 hour, whereas the moist fixed potassium increased with liming and was relatively soluble in 0.5 N HCl.

Similar changes in the exchangeable potassium level on drying of cropped soils were observed by Reitemeier et al (1948) who found that the potassium released, came from the clay fraction.

The potassium fixed on drying Mississippi delta soils was shown by Worsham and Sturgis (1942) to become exchangeable to a considerable extent when the soils were saturated with moisture showing that the potassium fixation on drying is not permanent but reversible.

Evans and Attoe (1948) cropping the above 6 Wisconsin soils with ladino clover, found that the soils with the highest potassium supplying powers were those which fixed the greatest amount of potassium on drying.

N.J. Volk (1934) found that the fixation of potassium on drying was widespread. Only 11 of 86 soils failed to fix potassium on being subjected to 10 cycles of wetting and drying at 70°C and 46 fixed more than one third of the applied potassium. He found that approximately 70% of the fixation occurred during the first cycle. In an examination of the fixation in the texture fractions, Volk found that only small amounts of potassium were fixed by the fractions coarser than 2 μ and then only by clay aggregates larger than 2 μ. The fraction S.G. $>$ 2.667 of the 0.3-2 μ fraction of Hagerstown silt loam, a strongly potassium fixing soil, showed on X-ray examination, increased lines which Volk attributed to muscovite, although muscovite is a hydrothermal mineral and is not likely to be formed in the soil (Kelley 1948). Little or no fixation of potassium by ground minerals including biotite, chlorite and some plagioclases was found.

G.W. Volk (1938) found that in the course of 20 cycles of wetting and drying at 70°C, no potassium was fixed by ground ($<$ 100 mesh) sericite, muscovite (3 samples) and negligible (4%) by kaolinite. 3 other muscovite samples fixed 9 to 17% and a white bentonite fixed 88% of added potassium.

*The term "potassium fixation" is used to imply the conversion of water soluble and exchangeable potassium into nonexchangeable forms.

Potassium fixation on drying was shown by Hauser (1947) to be widespread in Dutch soils with the exception of the potassium rich marine clays. The fixing power was credited to mica minerals. Terme and Marel (1954) and Marel (1954) reported that some Dutch soils have the power to fix added potassium so strongly that optimum yields of potatoes and of red clover were not obtained until after 8 years of annual fertilizing at 300 Kg K_2O per hectare (ca.5 cwt 60% KCl per acre). Of the potassium added over 16 years to one field at Ammerzoden, 59% was not used by the potato crop. Differences in the exchangeable potassium level accounted for 6% of this potassium, the remaining 53% being fixed in a nonexchangeable form. X-ray investigation showed that the soil at Ammerzoden contained a clay mineral in the $< 2\mu$ fraction of the same constitution as illite but with an expanding lattice like vermiculite. When potassium or ammonium were fixed by this mineral, the basal spacing contracted from 15.6 A for magnesium and calcium clays, to 10.8A for the potassium and ammonium clays, compared with a contraction quoted for vermiculite, from 15.6 A for the magnesium clay and 15.5 A for the calcium clay to 10.9 A for the potassium clay. No montmorillonite was present in the clay of the Ammerzoden field. Marel suggested the name "ammerzodite" for this illite-vermiculite-like potassium fixing clay. The potassium fixed by "ammerzodite" could be removed partly by $\underline{N}/20$ and $\underline{N}/10$ HCl. The remainder, approximately 2/3 of the fixed potassium, was bound so tightly that it was not removed by 10% HCl at room temperature.

Fixation of potassium during moist storage by a montmorillonite soil was shown by Raney and Hoover (1947) to account for 23% of 5.5me% of added potassium, a further fixation of 34% occurring on drying. Subsequent storage for one month, released some of the fixed potassium. Stanford (1948), by treating with HCl, acid washed illite clay and montmorillonite suspensions maintained for 48 hours at various pH's from 3.8 to 9.8 with NaOH, found that fixation with montmorillonite occurred only on drying, whereas with illite, rapid fixation occurred in the moist state with increased fixation on drying. Fixation in montmorillonite decreased with increasing pH to pH 6.5 after which it was constant, with illite, fixation both on moist contact and on drying, increased with the pH.

Similar effects of moist storage and drying were found by Allison, Kefauver and Roller (1953) for ammonium fixation, which is generally considered to take the same form as potassium fixation (Stanford and Pierre, 1947). Kaolinitic soils showed no fixation, montmorillonitic subsoils, a small moist fixation in 24 hours (< 1 me%) with up to 4 me% on drying, illitic subsoils 1.6-2me% moist and 6.7 me% on drying and vermiculitic subsoils 3-4 me% moist and 4.2-4.8 me% on drying. Surface soils showed smaller fixation capacities.

The high potassium and ammonium fixing power of some Californian soils was found by Barshad (1951) to be associated with the presence of vermiculite and vermiculite-biotite-chlorite intermediates. In distinction to the findings of Volk (1934), Barshad found that the coarser fractions, viz. coarse silt and sand, were capable of fixing ammonium ions, e.g. 85% of the ammonium fixed by a Sweeney soil was fixed by these fractions. Lightly ground vermiculite of 5-100 μ size was able to fix 150 me% K against replacement by ammonium ions and in so doing, changed into a "biotite". All this potassium was replaceable by magnesium ions in 2 days soaking, the "biotite" altering back to vermiculite.

Wear and White (1951) showed that $< 0.2\,\mu$ fractions of California bentonite, Wyoming bentonite, Putnam clay and illite, all fixed potassium on drying and attributed the potassium fixation to the formation of non-expanding layers in the mineral lattices, as shown by a lower 17.7 A peak in X-ray diffraction diagrams of glycerol solvated clays. They attributed variations between the minerals to the varying amounts of tetrahedral substitution of Aluminium for silicon, postulating that potassium was fixed only by these tetrahedral charges.

Barshad (1954) criticised Wear and White's conclusions on the dependence of potassium fixation on the presence of tetrahedral charges on the grounds that some vermiculites do not fix potassium although they have an appreciable tetrahedral charge density. He explains the absence of moist fixation in minerals with an interlayer charge of 70-130 me% on the basis of ease of accessibility into the lattices, which, because of the low charge density are easily expanded in water. The large fixation of ground minerals with a charge greater than 190 me% and with a contracted lattice, is explained by the large number of interlayer cavities and by the presence of an interlayer attractive force large enough to prevent expansion. He attributes the slight moist fixation shown by montmorillonites to the presence of small amounts of a vermiculite-like mineral of highish charge density. The known increase in fixation on drying is attributed to an increase in the interlayer attraction forces as the lattices contract during dehydration. The minerals then act as though they have a higher charge density. He claims that illites are actually clay size mixtures of potassium mica and a vermiculite with high interlayer charge (cf Jackson et al 1952).

Kunze and Jeffries (1953) found that where the clays from 15 Pennsylvania soils were potassium fixing, they showed a strong 10 A line for potassium clays compared with a strong 14 A line for magnesium clays. Where the potassium fixing power was weak, both clays showed 14 A lines. The former clays were shown to be vermiculite-like and the latter chlorite-like.

Brown (1954) comparing the clay minerals of Irish soils known to be potassium fixing and of those which did not fix potassium, found that whereas illite, vermiculite, chlorite and kaolin were found in varying proportions in all the soils studied, a mineral which, on glycerol solvation gave lines at 14 A and possibly at 10 A (masked by illite), was found only in those soils which fix potassium. He attributed all potassium in the field to the presence of this mineral which he called "degrading illite".

It may be seen from the above references that there is general agreement that the fixation of potassium on drying is a function of the clay fraction of soils and is associated with 2:1 layer lattice minerals, particularly of the clay-vermiculite - illite type.

EXTRACTION BY STRONG ACIDS

Practically all the estimates mentioned of potassium fixation or release as the result of some treatment, have been based upon changes in the amount of exchangeable potassium extracted before and after the treatment, the extractant used most frequently being N ammonium acetate, pH 7.0. The most commonly used rapid method for estimating the potassium supplying power of soils has been extraction by strong acids.

Although Kellner (Ref. Marel, 1954) used boiling N HCl to show that potassium fixed from potassium hydroxide was very strongly held by soils, the first to use strong acid as a fractionating agent, was Fraps (Ref. Reitemeier 1951), who boiled soil samples for 10 hours with HCl, S.G. 1.115.

Wood and DeTurk (1940) fractionated soil potassium after fixing added potassium, by leaching air dried samples with neutral N ammonium acetate and extracting 10 grams of the ammonium saturated residue with 100 ml. boiling N HNO_3 for 10 minutes. The potassium fixed in an acid-insoluble form was calculated by subtracting the potassium recovered from the potassium added. They found that a large proportion, which increased with increasing additions of potassium, of the added potassium was not extracted by the N HNO_3 treatment. DeTurk, Wood and Bray (1943) found incomplete extraction of fixed potassium from 5 of 6 Illinois soils by one N HNO_3 extraction. In all cases, except for the mature Cisne soil, there was a considerable increase in N HNO_3 soluble potassium where potassium had been fixed. There was a good correlation between the potassium extracted by the N HNO_3 and the known potassium status of the soils. From the non-potassium deficient Sable silty clay loam, the acid extracted 1.3 me% K, from the slightly potassium deficient Herrick silt loam, 0.7 me% K, and from the highly deficient Cisne and Wynoose silt loams 0.25 and 0.2 me % K respectively.

Variation in Acid Concentration

DeTurk, Wood and Bray (1943) in the above paper, reported that, for the Sable silty clay loam, the amount of potassium extracted by HNO_3 of varying concentrations increased up to 5 N, after which it became nearly independent of the acid concentration. Ayres (1949) found for Hawaiian soils that increasing amounts of potassium and sesquioxides were extracted by the more concentrated HCl solutions in the range N/2 - 4 N, when 25 gm. samples were extracted for 1 hour with 100 ml. of acid. A comparison between the non-exchangeable potassium removed on cropping and that soluble in N HNO_3 after the removal of exchangeable potassium by N ammonium acetate and N/20 HNO_3 for 12 soils showed that no significant correlation existed between them when the very high figure for the Makiki soil was omitted.

Temperature of Extraction

Although boiling acid has been used most frequently, prolonged soaking with cold acid was shown by Attoe and Truog (1945) and by Williams and Jenny (1952) to extract some nonexchangeable potassium, Williams and Jenny finding that nonexchangeable potassium was extracted in one week by N/10 acids only when the pH was less than 3.0.

Ratio of soil to acid and Time of Heating

Reitemeier et al (1948) digested 10 gram samples of soil with 100 ml. HNO_3 under varying conditions of concentration, temperature and time and found that the 1:10 ratio of soil to N HNO_3 with 10 minute boiling, provided the best correlation with ladino clover cropping uptake. The exchangeable potassium was not removed prior to digestion but was deducted from the acid extracted potassium. A correlation of 0.938 was obtained between 740 days ladino clover growth and this acid extraction figure. Rouse and Bertramson (1950) stated that the amount of potassium extracted by boiling N HNO_3 tended to level off as the boiling time increased and as the soil to acid ratio increased. They found that the best correlations with ladino clover growth were given by a ratio of 1:2 with 45 minutes boiling and by 1:10 ratio with 10 minutes boiling. The extraction at a soil to acid ratio of 1:2 was very sensitive to dilution but not to time, whereas the 1:10 ratio was not sensitive to dilution but was very sensitive to variations in the time of boiling. Because it is easier to control time accurately than to control dilution, they recommended a boiling time of 10 minutes at a soil to acid ratio of 1:10 with the prior removal of exchangeable potassium by leaching with N/5 HNO_3.

Size of Soil Sample

The amount of soil extracted was reduced by Pratt (1951) from 10 grams to 2 grams and the ratio of soil to acid changed for 1:12½. The exchangeable potassium was not removed before extraction which was of 10 minutes duration after a cold soaking for 15 minutes.

Extraction of Minerals

The effect of boiling strong acid on the various soil forming minerals varies considerably. Biotite was reported by Marel (1947) and others to be completely soluble in 20% HCl on boiling. Rouse and Bertramson (1950) were able to extract from minerals, after ball milling, removal of exchangeable potassium formed and saturation with calcium, the following amounts of potassium by boiling for 10 minutes with N HNO_3 at a mineral to acid ratio of 1:10, as shown in the accompanying table. The results are expressed in me K %.

SIZE OF FRACTIONS

Mineral	53-20μ	20-5μ	5 - 1μ	1 - 0.2μ	$<0.2\mu$
muscovite	1.6	2.5	4.0	$< 5\mu$	
Microcline	0.6	1.4	2.5		
Glauconite	4.0	4.8	4.8		
illite					5.7
Soil separates	0.3-0.5	0.5-1.3	1.1-5.0	2.0-5.0	0.7-4.6
Average for 16 soils	0.4	0.65	1.4	3.3	3.1
minerals in soil separates	microcline		Quartz Muscovite Chlorite	Illite Chlorite and some Montmorillonite	Secondary micas (illite ?)

Although on a unit weight basis, most of the potassium came from the clay $<1\mu$, because of the predominance of silt and sand, half of the potassium extracted from the whole soil came from the clay and half from the silt plus sand.

They found no relationship between the felspar content and the potassium supplying power of the coarser fractions although Phillippe and White (1952) using the same soils found a significant relationship between the microcline content (range 9-16%) of the silt fraction and the acid soluble potassium. Rouse and Bertramson also found no relationship between the illite-muscovite peak in the coarse clay and the potassium supplying power but found that the potassium supplying power was correlated with size of the illite peak for the medium and fine clay where the samples were not dried before solvation (correlation coefficients of 0.94 and 0.82 respectively).

Pratt (1952) in a further study on Iowa soils, after fractionating them into 20, 20-10, 10-5, 5-2, 2-0.2 and $< 0.2\mu$ sizes, extracted the size fractions at a ratio of 1:12½ and found that appreciable amounts of potassium were extracted from all fractions. With soils derived from glacial till, the $<0.2\mu$ and 0.2-2μ fractions released equal amounts of potassium (about 2 me%) with rapidly decreasing amounts of potassium from the coarser fractions, fine silt 1.0 me%, coarser silts 0.5 and 0.35 me% and fine sand 0.27 me%. A highly weathered Planosol was similar to the glacial till soils but with about half the extraction values. The soils derived from loess gave the greatest releases with the 0.2-2μ fraction (about 1½ times the release from the $<0.2\mu$ fraction). The coarser fractions behaved similarly to the glacial till soils. Although the soils were fairly sandy, between 40 and 75% (average 60%) of the potassium released came from the clay fraction, 16-28% (ave. 24%) from the silts and 8-32% (average 16%) from the sands. The accumulated weighted release from the fractions was less than the potassium released by the whole soil in every case, the deficiency being from 4 to 28% (0.54 me% on 1.98 me%). The percentage difference was positively correlated with the potassium released from the whole soil. Pratt ascribed the difference to a loss of potassium brought about by release during fractionation.

Multiple Extractions

Although it was improbable that all the acid soluble potassium was extracted in one extraction, DeTurk, Wood and Bray (1943) were the only workers prior to Metson to extract the $\underline{N}$ HNO_3 treated residue with further acid. They boiled the residue from a 10 minute $\underline{N}$ HNO_3 digestion with $5\underline{N}$ HNO_3 for 10 minutes (1 gram of residue to 10 ml. acid) and found that further potassium was extracted. In studying fixation by clay of <0.06, 0.06-0.1 and 0.1-1μ, they found that the first extraction was affected by fixed potassium but the second was more or less independent of the fixation.

Evans and Simon (1949) subjected 7 Ohio and Wisconsin soils to a series of 6 wetting and drying cycles with intervening extraction of the exchangeable potassium by cold $\underline{N}/2$ HCl or by $\underline{N}$ ammonium acetate, pH 7. Potassium was released at rates which varied considerably. They claimed that their data fitted straight line of gradients approximating to the observed release on cropping, although by inspection of their data, it is apparent that the amount of potassium released per extraction decreased steadily. The amounts of potassium extracted were small, less than 0.5 me% in 6 extractions, compared with $\underline{N}$ HNO_3 extracts of up to 2.0 me% from similar soils as reported elsewhere.

Metson and Hurst (1953) attempted to get a better idea of the potassium supplying power by repeating the $\underline{N}$ HNO_3 extraction to give 4 extractions, with a soil to acid ratio of 1:12½ and a boiling time of 10 minutes. The exchangeable potassium was not removed prior to the first $\underline{N}$ HNO_3 extraction. For samples of Wakanui silt loam taken from a 4 year grazing trial, approximately 0.8 me% K was extracted in all extractions after the first, which, after the subtraction of the exchangeable potassium, averaged about 1.35 me%. They were unable to trace the source of 2.2 and 3.0 me% of potassium which were removed during the trial. Metson (1954) extended the investigation on multiple extraction of soils to cover the main New Zealand soil groups and found that for many soils, a more or less constant rate of extraction prevailed after the second extraction. Wide differences up to fifty fold variation, were found between soil groups, with a general similarity apparent between the curves for soils of the same genetic group. He grouped the soils according to the rate of constant extraction into high, medium and low to very low. His low to very low group included the majority of the soils on which potassium responses have been observed in New Zealand. He obtained no correlation between exchangeable potassium and $\underline{N}$ HNO_3 soluble potassium.

Nitric acid soluble potassium and plant uptake

The level of potassium at which potassium deficiencies become marked appears to be 0.15 me % for exchangeable potassium. Legg and Beacher (1952) found for Arkansas soils with exchangeable potassium from 0.1 to 0.3 me%, that where the $\underline{N}$ HNO_3 soluble potassium figure was > 0.65, potassium deficiencies were not found.

Schmitz and Pratt (1953) found that to a heavy dressing of K Cl yield responses greater than 25% were not found unless the $\underline{N}$ HNO_3 soluble potassium (including exchangeable potassium) was less than 1.0 me%. They found that the best correlation between plant uptake of potassium and soil potassium was given by the multiple regression

$$\hat{Y} = 2 + 0.946 X_1 + 0.195 X_2$$

where $\hat{Y}$ is the total potassium removed by cropping,
X_1 is the exchangeable potassium before cropping and X_2 the release of potassium to $\underline{N}$ HNO_3.
The multiple correlation coefficient for this regression was 0.959.
Semb and Uhlen (1955) found for Norwegian soils that while there was virtually no correlation between exchangeable potassium and $\underline{N}$ HNO_3 soluble potassium, the best correlation between potassium uptake and soil potassium was given by

Calculated uptake = k (exchangeable K + 15% $\underline{N}$ HNO_3 soluble K).

Nitric acid is thus seen to be capable of extracting non-exchangeable potassium from soils and ground minerals in amounts which are related closely to their potassium supplying powers.

ELECTRODIALYSIS

The other rapid laboratory method for estimating potassium supplying power of soils is electrodialysis. Ayres (1949), Reitemeier et al (1951) and Pearson (1952) electrodialysed soils for periods from 1 to 40 days and were able to obtain good correlations between the non-exchangeable potassium extracted by crops and by electrodialysis. In most cases, the exchangeable potassium was extracted in 1 day and for the next 7 days or so, continuously decreasing amounts of potassium were extracted, after which a nearly constant rate of extraction occurred. Any potassium fixed prior to electrodialysis was extracted during the period of continually decreasing rate of extraction, suggesting that the fixed potassium was more readily removed than the native potassium.

POTASSIUM STATUS OF NEW ZEALAND SOILS

The little published information available on the potassium status of New Zealand soils is mainly field trial data from potassium fertiliser trials. According to During (N.Z. 1953) soils derived from volcanic ash are almost without exception potassium responsive, as are soils in Northland derived from semi-basic and basic volcanic rocks. Strongly weathered yellow brown earths derived from sandstones other than greywacke also show responses, as do some recent alluvia in high rainfall areas. Apart from organic soils which are always potassium responsive in the North Island and frequently so in the South Island, only scattered slight responses have been recorded.

To secure further information on the potassium supplying power of New Zealand soils, this study was carried out, using a wide range of soils, cropping them with Italian ryegrass, and determining the amount of potassium

L. I. GRANGE
DIRECTOR

Soil Map
of
NEW ZEALAND

1948

Scale 1:2,027,520

To accompany bulletin No. 3
"A Genetic Classification of New Zealand Soils"
by N.H. Taylor.

Compiled from surveys by
H.S. Gibbs, L.I. Grange, C.S. Harris,
I.J. Pohlen, J.D. Raeside, C.F. Sutherland,
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of the Soil Bureau, Dept Scientific
and Industrial Research.
New Zealand.

POTASSIUM STATUS.

Responsive	▧
Slightly Responsive	▨
Not Responsive	▥
Unknown	☐

According to Burgess and Bell (1952)
Modified on Information supplied by During (Pers.Comm.)

LOCATION OF AREAS SAMPLED.

New Plymouth sandy loam	3
Taupo sand	2
Kiripaka clay loam	1
Middlehurst silt loam	9
Tokomaru fine sandy loam	6
Omakere clay loam	4
Idaburn fine sandy loam	12
Timaru silt loam	11
Halcombe silt loam	8
Matamau silt loam	7
Waipara silt loam	10
Himatangi coarse sand	5

removed. The source of this potassium was traced by extracting samples of the soils, their texture fractions and separates of different specific gravities, with boiling normal nitric acid. The conditions of acid extraction were examined critically to ensure that a reasonably specific method for available non-exchangeable potassium was developed.

EXPERIMENTAL SECTION

MATERIALS AND METHODS

DESCRIPTION OF SOILS

The soils used in this study were topsoils, i.e. A horizons, selected on the basis of their exchangeable potassium and N HNO_3 soluble potassium contents determined by the method of Wood and DeTurk (1940) as modified by Pratt (1951). They were selected to give the following combinations of exchangeable potassium and acid soluble non-exchangeable potassium.

Exchangeable potassium	Non-exchangeable potassium	Soil selected
Low	Low	Soil C
Medium	Low	Soil A
High	Low	Soil B
Low	Medium	Soils H, R
Medium	Medium	Soils I, K, O, P
Medium	High	Soils G, M, Q

A brief description of the soils chosen, together with the location of the sampling sites (see also Figure 1) is as follows.

The soil types refer to the General Survey of the Soils of the North Island, N.Z., Soil Bureau Bulletin (n.s.) 5 (1954) and the figures in brackets refer to the Genetic Classification Groups of Taylor (1948) as given in the table on the 32 mile to the inch map in Figure 1.

Soil A. New Plymouth sandy loam, type 67b (14a).

Yellow brown loam, derived from Stratford ash and Egmont ash, of andesitic origin.
Topsoil 6-8 in. dark brown friable sandy loam on yellowish sandy loam.
Location of sampling: Paddock at rear of Tikorangi School.
Previous History: Farmland, ploughed 7 years previously, 1 cwt. 60% KCl per acre in spring before sampling.
Sampling date: 6 - 2 - 53.

Soil C. Taupo sand, type 18b (13a).

Yellow brown pumice sand, derived from Taupo ash (rhyolitic).
Topsoil 3 in. dark grey sand, on yellowish brown sand.
Location of sampling: Grassland Experimental Plots, near Wairakei.
Previous History: Virgin soil, manuka scrub.
Sampling date: 20 - 3 - 53.
Collected by an Officer of Grasslands Division, D.S.I.R.

Soil E. Kiripaka clay loam. type 95 (16a).

Red brown loam, derived from basalt.

Topsoil 5 in. very dark grey brown, heavy silt (clay) loam, friable, moderately developed fine-medium granular structure, with very compact subsoil.

Location of sampling: 1 mile South of Maungakaramea, Whangarei County.

Previous history: Virgin soil, cocksfoot, bracken, blackberry, lotus major.

Sampling date: 13 - 1 - 53.

Collected by C.F. Sutherland, Soil Bureau, D.S.I.R.

Soil G. Middlehurst silt loam. (16a).

Red brown loam, derived from basalt. The presence of orthoclase and quartz in the fine sand would indicate considerable admixture with sedimentary material probably loess.

Topsoil 6 in. dark red brown gravelly silt loam.

Location of sampling: 1½ miles North of Gladstone Bridge, Awatere Valley, Marlborough.

Previous history: Tussock, potassium fertilizers very unlikely.

Sampling date: 10 - 2 - 53.

Collected by M. Gradwell, Soil Bureau, D.S.I.R.

Soil I. Tokomaru fine sandy loam. type 15 (2f).

Yellow grey earth, derived from alluvium.

Topsoil 6 in. dark brown grey fine sandy loam on yellowish grey clay loam.

Location of sampling: Clifton Terrace, Massey Agricultural College.

Previous history: Original bush burn pasture, no topdressing of any kind.

Sampling date: 23 - 4 - 53.

Soil K. Omakere clay loam. type 29 (5G), grouped with Atua silt loam in 4 mile to inch survey.

Yellow brown earth, derived from mudstone.

Topsoil 6 in. dark brown grey clay loam on yellow brown clay.

Location of sampling: 1 mile along Atua Road from Waipawa to coast road, from small nob near Omakere Stream.

Previous history: Original browntop, danthonia, mossy sward, no topdressing.

Sampling date: 23 - 7 - 53.

Soil M. Idaburn fine sandy loam. (1a).

Brown grey earth, derived from mica schist.

Topsoil 8 in compact brown grey fine sand on grey brown gravelly sand.

Location of sampling: Roadside near Burnt Cottage Creek, Cromwell-Lindis Road, Central Otago.

Previous history: Unknown, potassium fertilizers very unlikely.

Sampling date: 31 - 1 - 54.

Soil N. Timaru silt loam. (2c).

Yellow grey earth, moderately gammate, moderately leached, tussock melanised, derived from loess.
Topsoil, 8 in. dark grey moderately crumbly silt loam on yellow compact subsoil.
Location of sampling: Roadside cutting, corner of Morgan's Road and Gleniti Road, Timaru.
Previous history: Under gorse, potassium fertilisers unlikely.
Sampling date: 2 - 2 - 54.

Soil O. Halcombe silt loam. type 13 b (2g).

Yellow grey earth derived from sandy mudstone.
Topsoil 7 in. dark grey silt loam on yellowish grey clay loam.
Location of sampling: Roadside cutting, corner of Moiki Road and Morison's Bush Road, Featherston, South Wairarapa.
Previous history: Under browntop and danthonia, Potassium fertilizers unlikely.
Sampling date: 7 - 2 - 54.

Soil P. Matamau silt loam. hill soil, type 77 H (14a).

Yellow brown loam, derived from pumiceous sandstone and mudstone.
Topsoil 5 in. brown granular silt loam on yellow brown granular silt loam.
Location of sampling: Roadside cutting, ½ mile on Manawatu side of the summit of the Pahiatua Track.
Previous history: Browntop dominant pasture, potassium fertilizers very unlikely.
Sampling date: 5 - 4 - 54.

Soil Q. Waipara silt loam. (2b).

Yellow grey earth, derived from greywacke silts and loess.
Topsoil 10 in. dark grey silt loam on pale yellow silt loam.
Location of sampling: Waikari Valley, North Canterbury.
Previous history: Roadside browntop, cocksfoot and flatweeds, practically undisturbed. Potassium fertilizers unlikely.
Sampling date: 10 - 6 - 54.
Collected by J.P. Fox, Soil Bureau, D.S.I.R.

Soil R. Himatangi coarse sand. type 23 (12).

Yellow brown sand, derived from dune sand.
Topsoil 4 in. dark grey black coarse sand on light grey coarse sand.
Location of sampling: Lake Road, Oroua Downs, Manawatu.
Previous history: Mixed grasses and subterranean clover. No potassium fertilizers.

Further data concerning these soils is given in Table 3. The location of the above sampling sites is shown on the map in Figure 1.

PREPARATION OF LABORATORY SAMPLES

Samples of approximately one hundred pounds of the topsoils of the above list of soils were collected, air dried, and mixed. 25 pound subsamples were ground lightly and plant remains removed. Stones (> 2mm) were sieved from the soils, Taupo sand and Kiripaka clay loam where they made up only a small fraction but were left in the Middlehurst silt loam where they made up about 30% by weight.

Approximately 4 pounds of these lightly ground samples were taken for laboratory tests, again ground lightly and sieved through a 2mm sieve. That portion passing the sieve (fine earth) was retained.

DETERMINATION OF PHYSICAL PROPERTIES OF SOILS

The following methods were used to determine the data of Table 3.

Moisture content of air dried sample. The moisture content of the air dried soil was determined by drying 10 gm. samples for 12 hours at 110°C.
Note: All results in this study are expressed on the basis of oven dried sample weights, calculated on the basis of these determinations.

Loss of ignition at 800°C. The oven dried samples from the above determinations were ignited at 800°C for 30 minutes and reweighed.

Mechanical Analysis.
Method A. 10 gm. samples of the soils were dispersed according to the International method (Wright 1949) using H_2O_2 to destroy organic matter and ammonium hydroxide as the dispersing agent, as recommended by Davies (1958).
Method B. In the preparation of samples of the texture separates for laboratory tests, varying amounts of soil were treated with H_2O_2 to destroy organic matter, dilute nitric acid was added to the cooled solution, and after 30 minutes, the supernatant liquid decanted and the residue washed with water and centrifuged. The residues were dispersed using calgon and sodium carbonate. The fractions were separated by sedimentation for the appropriate times and the clay precipitated by the addition of magnesium chloride solution to the alkaline solution.

Clay minerals. Fieldes and Williamson (1955) summarized the results of the survey of the clay minerals of New Zealand soils. The list of probable clay minerals of the 12 soils used for cropping, as shown in Table 4, is taken from this paper and confirmed by Fieldes (personal communication).
Minerals of the coarser fractions.
Deferration. Samples of the fine sand fractions from the mechanical analyses, Method B, were deferrated by the method proposed by Matelski (1953) using a series of detergents. This method was chosen because it was very efficient in removing the weathered coating from the mineral surfaces and because it appeared to be less destructive than the acid-nascent-hydrogen methods recommended by other workers.

TABLE 3.

PHYSICAL PROPERTIES OF THE SOILS USED FOR CROPPING

Soil	Group	H_2O in air dry soil	Loss on ignition at 800°C	% clay	% silt	% fine sand	% coarse sand
		%	%	%	%	%	%
New Plymouth sandy loam	YB loam	19.8	27.3	14.1	10.2	31.3	10.1
Taupo sand	YB pumice soil	3.8	10.7	2.9	12.3	56.2	19.4
Kiripaka clay loam	RB loam	16.7	25.0	46.7	10.8	12.3	1.5
Middlehurst silt loam	RB loam	6.8	8.4	20.6	32.2	32.8	15.9
Tokomaru fine sandy loam	YGE	4.5	9.1	22.0	24.2	44.3	0.5
Omakere clay loam	YBE	6.5	10.3	32.7	32.5	23.2	1.8
Idaburn fine sandy loam	BGE	0.9	3.1	7.5	14.5	62.0	10.7
Timaru silt loam	YGE	3.5	9.2	16.6	30.3	43.2	0.8
Halcombe silt loam	YGE	7.6	7.4	16.4	28.9	44.7	1.5
Matamau silt loam	YB loam	4.0	12.2	20.6	26.7	26.4	4.9
Waipara silt loam	YGE	1.7	7.7	18.0	25.9	43.8	5.4
Himatangi coarse sand	YB sand	2.5	4.8	2.4	2.4	42.3	46.5

TABLE 4

MINERALOGICAL DISTRIBUTION IN THE SOILS USED FOR CROPPING

Soil	Group	Probable clay minerals $< 2\mu$, in order of abundance.	Fine sand minerals in order of abundance.
New Plymouth sandy loam.	YB loam.	Allophane A, Meta-halloysite Iron oxides, felspar.	Hornblende, augite Basic plagioclase.
Taupo sand.	YB pumice soil.	Allophane AB Glass, Felspars.	Glass Quartz Hornblende.
Kiripaka clay loam.	RB loam.	Fine particle size gibbsite, Meta-halloysite, crystalline oxides.	Partially weathered olivine and augite.
Middlehurst silt loam	RB loam.	Amorphous hydrous oxides, Micaceous material, Palagonite.	Iron ores Augite, hornblende Andesine, quartz and orthoclase Brown chlorite Celadonite (?)
Tokomaru fine sandy loam.	YGE ✓	Low K illite, possibly a collapsed clay-vermiculite.	Quartz, Orthoclase, ✓ Glass, Plagioclase.
Omakere clay loam	YBE	Mixed and interlayered hydrous micas Montmorillonite from parent material.	Quartz, Plagioclase, Orthoclase, Glass.
Idaburn fine sandy loam.	BGE	Weakly hydrated mica Hydrous micas.	Albite, quartz, Epidote, hornblende, Chlorite, biotite, Muscovite.
Timaru silt loam	YGE ✓	Hydrous micas, predominately illite.	Quartz, Orthoclase, ✓ Plagioclase, Chlorite.
Halcombe silt loam.	YGE ✓	Hydrous micas, predominately illite, collapsed vermiculite.	Quartz, Andesine, orthoclase, ✓ Glass.
Matamau silt loam.	YB loam.	Allophane A Micaceous clay.	Quartz, Glass, Orthoclase.
Waipara silt loam.	YGE ✓	Hydrous micas, predominately illite.	Quartz, Orthoclase, ✓ plagioclase, Chlorite.
Himatangi coarse sand.	YB sand.	Unknown, probably includes illite.	Quartz, andesine, Augite, hornblende, Hypersthene.

The sample of 2-10 gms. was triturated for 3 minutes with about 0.1 gm. Triton K-60 and 0.1 gm. Triton X-100 and 10 ml water in a porcelain mortar using a rubber bung mounted on a screwdriver as a pestle. The rubbed mixture was washed into a beaker, made up to 10 cm. and the silt and clay decanted twice after 5 minute intervals at 20°C. This treatment was repeated once and the remaining fine sand particles were rubbed with 0.5 gm. calgon, 0.5 gm. tetrasodium pyrophosphate, 0.5 gm. $NaSiO_3$ and 0.2 gm. teepol in 10 ml water for 2-3 minutes. Water was added to the mixture and the silt and clay decanted as before. This treatment was repeated twice or until, under the microscope, the particles appeared clean and separate. The deferrated fine sand was then dried at 105°C.

A similar procedure was used for deferrating the silt fraction but with only one trituration with each set of detergents.

Specific gravity separations. The deferrated fractions were separated into fractions of different specific gravities by sedimentation in tetrabromoethane - acetone mixtures of known specific gravities. Between 2 and 10 gm. of a fraction was stood in a separating funnel or centrifuge tubes with tetrabromoethane-acetone mixtures of the desired specific gravity until a separation into sunk or floating particles had been achieved. Preliminary evacuation to about 40 cm. vacuum was necessary to remove any air absorbed on the surface of the mineral particles. After the separation, the particles floating at the surface were sucked off at the pump into a flask. Although an incomplete separation is achieved by a single treatment, after 4 or 5 repetitions, a reasonable separation is made.

The specific gravity separates were recovered by diluting the tetrabromoethane-acetone mixture with acetone and after decanting, washing the residue with further acetone. The tetrabromoethane was recovered from the acetone washings by pouring into a large volume of water, in which the acetone alone is soluble and decanting the acetone-water mixture. Any traces of acetone remaining were removed by washing the tetrabromoethane with water.

The tetrabromoethane used was prepared by the method of O'Meara and Clemmer (1929) by bubbling acetylene into bromine containing a small amount of water, until the bromine was decolourized. After washing with water to remove traces of bromine and acetylene, the specific gravity was found to be 2.96.

The acetone used was commercial acetone, specific gravity 0.79.

The tetrabromoethane-acetone mixtures were prepared using the formula

$$\text{Weight acetone required} = 0.79\,\frac{(2.96 - d)\ \text{wt.}}{(d - 0.79) \times 2.96}\,_{\text{TBE}}$$

where d = specific gravity required

wt._{TBE} = weight of tetrabromoethane taken.

The specific gravity of the liquid was checked and adjusted if necessary.

Determination of Fine Sand Minerals

The mineral species present in the fine sand fractions of the soils were identified by determining the following properties under the microscope:

Colour, refractive index, birefringence, isotropic character and pleochroism.

The list of minerals determined and reported in Table 4, was confirmed and corrected where necessary by J. Reed, Geological Survey, D.S.I.R.

REAGENTS.

All reagents used were of ANALAR grade unless otherwise specified. The distilled water and reagents were tested for their potassium content and any potassium found was allowed for in calculating results.

GLASSHOUSE INTENSIVE CROPPING EXPERIMENT

In order to observe the effects of intensive plant growth on the various forms of soil potassium, the 12 soils described on pages 24-27, were cropped with Italian ryegrass (lolium multiflorum) of a biennial strain, supplied by the Grassland Division, D.S.I.R., from April-July 1953 for soils A-K and from April-June 1954 for soils M-R until November 1955. In order to avoid complications arising from competition between plant species, a single species crop was preferred to a mixed one. Italian ryegrass was chosen for cropping in preference to the plants used by most U.S.A. workers, e.g. ladino clover or oats for the following reasons.

1. It is a strongly growing species, particularly during the colder months. Most of the pots were sown down in the Autumns of 1953 and 1954 and as rapid as possible establishment was desired.
2. Its growth is not affected by variations in nodulation as with the legumes.
3. It has a longer growth period and is more persistent than oats or other cereals.

If the work of Mitchell (1955) on the depressing effect of temperatures in excess of 70°F on the growth of ryegrasses had been known when the experiment was started, it is probable that some other grass, e.g. cocksfoot, would have been chosen instead.

The pots which held just over 1 Kg. of air dry soil, were made from tinned containers 14 cm. high and 14 cm. in diameter. A 1 cm. hole was punched in the base to allow for drainage and the tin spray painted with 2 coats of clear spirit varnish. The drain hole was covered with a disc of copper sheet approximately 3 cm. in diameter and sufficient acid washed gravel (> 3 cm.) was added to ensure good drainage. The weight of the containers was adjusted to 350 gm. with this gravel.

Air dried soil, which had been mixed with the requisite amount of basal fertilizer mixture, was then added equivalent to 1 Kg. of oven dried soil per pot to 3 pots for each soil. (Note 1 Kg. gravel was added to the

Middlehurst silt loam to give a reasonable volume of soil. The pots of New Plymouth sandy loam and of Kiripaka clay loam contained air dry soil equivalent to 810 gm. and 340 gm. oven dry soil).

The basal fertilizer dressing was:

P as	Na H_2PO_4	Analar	grade.	150 mgms.
N	NH_4NO_3	"	"	200 "
Fe	$FeSO_4 \cdot 7\ H_2O$	"	"	100 "
Cu	$CuSO_4 \cdot 5\ H_2O$	"	"	5 "
Mn	$MnSO_4 \cdot 6\ H_2O$	"	"	5 "
B	H_3BO_3	"	"	5 "
Zn	$ZnSO_4 \cdot 7\ H_2O$	"	"	5 "
Mo	ammonium molybdate			0.25 "
S	$FeSO_4 \cdot 7\ H_2O$ above.			

Ca and Mg as a 2 $CaCO_3$: $MgCO_3$ mixture, 1 gm. per 2000 lb. lime requirement as determined by the method of Woodruff (1943).

All fertilizers and the distilled water were analysed for potassium and it is considered that less than 50 mgms. of potassium per pot (0.01 me K %) were added from these sources.

The soils were wet to field capacity, stood for 12 hours and planted with 12 Italian ryegrass seeds and transferred to an unheated glass house. Any water draining through the pots after this and after subsequent waterings was collected and returned to the surface of the soil.

After 2 weeks the seedlings were adjusted to 4 per pot either by thinning or by transplanting. Regular watering with distilled water was carried out so that the pots were maintained at or near field capacity. Dressings of $NH_4H_2PO_4$ and NH_4NO_3 were made at irregular intervals and the soils were "limed" 3 times with the $CaCO_3$: $MgCO_3$ mixture, the dressings being determined by Woodruff's test.

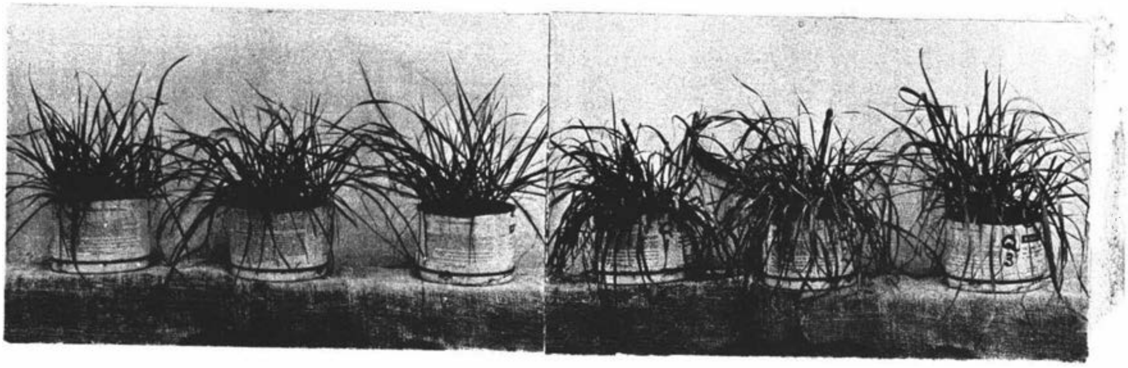
The grass, cut at 3 weekly intervals at approximately 3 cm. from the soil surface, was dried and weighed to give the yield of dry matter. Approximately 1/4 gm. aliquots of ground or shredded dried grass were taken for potassium analyses.

The plants were sprayed regularly with dilute "Hexone" in water to kill aphides, thrips and mealy bug which infested the grass. Even with this spraying, under the conditions prevailing in the glasshouse, it was difficult to prevent infestation by these pests and aphides and mealy bug appeared frequently.

It was found that considerable root development took place and that in many pots, roots appeared through the drain hole. Where the soil tended to become pugged by adding water to the soil surface, in particular, the pots of Tokomaru fine sandy loam and of Omakere clay loam, water was added to

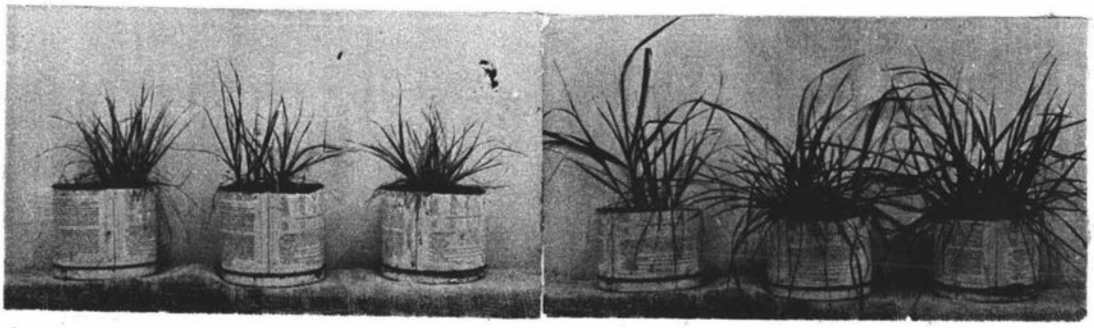
FIGURE 6.
SELECTED PHOTOGRAPHS OF GLASSHOUSE POT EXPERIMENT.

General View of Glasshouse.



Typical First Year's Growth. Halcombe Silt Loam and
Waipara Silt Loam. Oct.1954.

Mode of Death of Plants. Note small amount of regrowth
from previously healthy plant.



Typical Second Year's Growth. Middlehurst Silt Loam and
Tokomaru Fine Sandy Loam.
Oct.1954.

the drainage collecting dish from whence it was taken up by the roots.

10 gm. samples were taken at 6 monthly intervals for exchangeable potassium and for acid soluble potassium determinations by taking 4 cores with a 1 cm. cork borer. The cores were quartered and the surplus three quarters were returned to the pots.

Selected photographs of the pots are shown in Figure 5 to illustrate the general appearance of the pots and glasshouse.

METHODS FOR THE ESTIMATION OF POTASSIUM

The standard gravimetric, volumetric and colourimetric methods for determining potassium are all time consuming and require accurate and reproducible control over experimental conditions to ensure a high degree of accuracy. Variations in the composition of the precipitate and incomplete removal of excess reagent by washing are but two of the many causes of variation which occur with the cobaltinitrite method.

In addition, the standard methods are not all specific for potassium and are influenced to varying degrees by other ions, in particular by ammonium, barium, ferric, aluminium and phosphate ions (Tinsley, 1948).

FLAME PHOTOMETRY

The method which has become almost universal because of its speed, accuracy and specificity is the estimation of potassium by measuring the intensity of the radiation emitted at 769 mμ by potassium atoms when they are excited in a flame.

The method of estimation consists essentially of measuring the radiation emitted at 769 mμ, when potassium is introduced into a flame under controlled uniform conditions, so that variations in the potassium concentration of the solutions tested, are reflected proportionately in the intensity of the radiation.

The equipment necessary to achieve this, consists of two parts, the first, apparatus which will produce the radiation and the second, apparatus which will measure the radiation. Together, they are called a flame photometer.

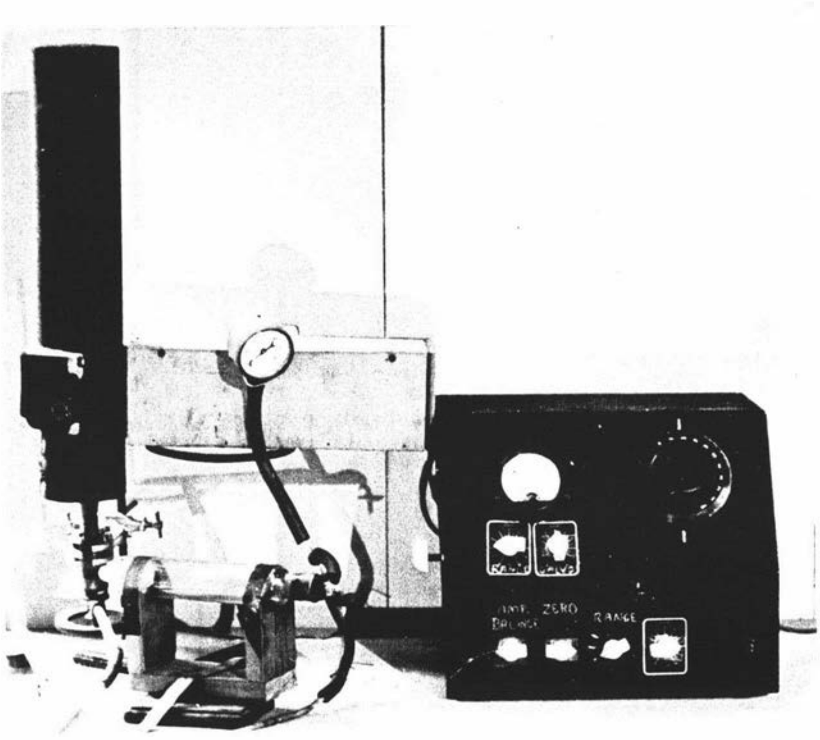
The most convenient and reliable method of producing potassium radiation is to atomise a solution containing potassium and to blow the spray into a flame produced under standard conditions. For accurate determinations, the following conditions must be standardized for the reasons given.

Flame.

Type of combustion mixture.	Gases burn at different temperatures with consequent variations in excitation. The proportion of oxygen in the flame also affects the temperature, therefore a standard gas - oxygen (air) mixture must be burnt.
Gas pressure and amount of air or oxygen reaching the flame.	The intensity of radiation from any part of the flame size, depends on the flame size, which is dependent on

FIGURE 7.

PHOTOGRAPH OF FLAME PHOTOMETER.



	these variables. Also it is essential that the no-potassium flame be colourless and that no Swan bands for carbon are present as one of these produces radiation at 769 mμ.
Flame size.	Because of fluctuations produced by flickering of the flame edges, these are usually screened off by a diaphragm thus exposing only a portion of the flame.

Atomizing.

Air pressure.	A fixed rate of atomizing is essential. The all glass atomizer produced by the Beckman Corporation produces a spray which is nearly uniform under a moderate range of air pressures. The limiting factor in the atomizing rate at air pressures above 15 pounds per square inch, is the size of the capillary liquid feed.
Temperature and viscosity of the solutions.	Variations in viscosity of the solutions to be atomized, because of their effect on the rate of flow through the capillary liquid feed, affect the atomizing rates. Variations in the temperature of the solutions must be avoided because of the dependence of the viscosity on the temperature.

The second part of the flame photometer may be any form of radiation measuring apparatus with a suitable monochromator to eliminate undesirable illumination.

The two most commonly used forms are

1. A barrier layer photocell connected directly to a suspension galvanometer.
2. A phototube, either vacuum or gas filled, with an amplifier of the null point or direct reading type. These may be made more sensitive than type 1 and are used in the more sensitive flame photometers.

The monochromator may be of the quartz prism or diffraction grating type or of the filter type. The former are more selective and flexible than the filter type and are essential if more than one element is to be determined but the filter type is quite suitable for single element determinations.

CONSTRUCTION OF FLAME PHOTOMETER

As no flame photometer was available, the instrument shown in Figure 7 and described below, was designed and constructed, incorporating features calculated to eliminate as many of the above causes of variation as possible.

Atomizer and Flame Unit

A Beckman type all glass atomizer was mounted in a copy of the Beckman atomizing chamber, which led into the bottom of a Meker burner

(Fisher type) immediately above the gas jet (see Figure 7).

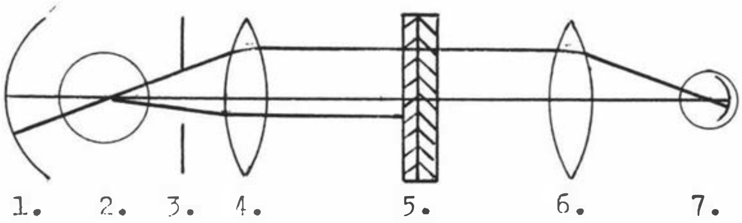
Compressed air was fed from a high pressure cylinder through a diaphragm pressure reducing control unit to give a pressure of 20 p.s.i. the atomizer air intake. This pressure was chosen because it was well ab the minimum required air pressure, viz. 15 p.s.i. and it gave a reasonable atomising rate and with the additional air, which was sucked through the ai intake tube into the atomising chamber by the air jet, this pressure gave a colourless no-potassium flame large enough to fill the aperture in the optical system.

The fuel used was Rockgas, a commercial propane-butane mixture, at a pressure of 0.5 p.s.i., the pressure being controlled by a diaphragm pressure reducing control unit and a needle valve.

<u>Photometer</u>

The radiation produced in the flame was collected and filtered by the optical train shown in Figure 8.

<u>F I G U R E   8</u>

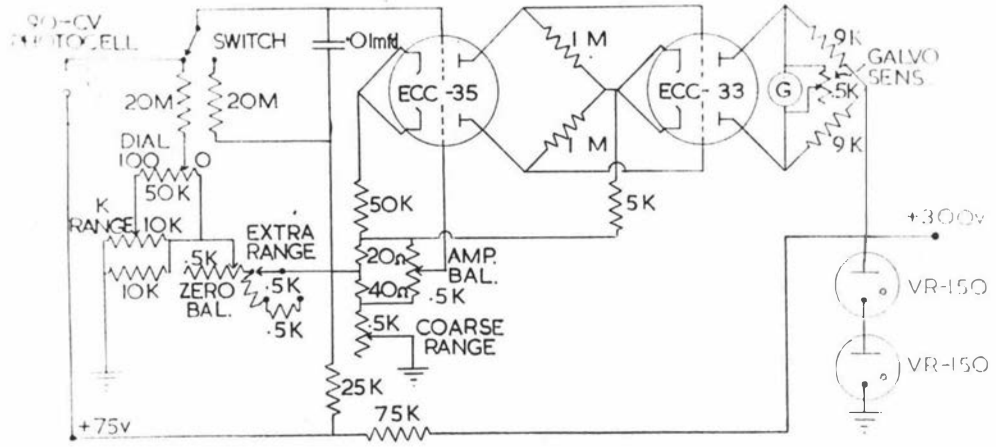


1. Cylindrical mirror.
2. Flame.
3. Diaphragm.
4. Condensing lens.
5. Filters, Ilford 606 + 60
6. Condensing lens.
7. Red sensitive photocell.

<u>Diagram</u> of the optical train of flame photometer.

The radiation after filtering, was focussed on the red sensitive phototube, type Philips 90-CV, producing variations in its resistance depending on the intensity of the illumination. These variations were measured by a modified Wyn-Williams bridge circuit with twostage amplification, altered slightly from the design of Schoene, published by Bills, McDonald, Niedermeier and Schwartz (1949). The circuit as used is shown in Figure 9. The instrument proved very sensitive, accurate and easy to work.

FIGURE 9.



Amplifier Circuit

CALIBRATION OF FLAME PHOTOMETER

In Table 5, the readings (actual dial - water blank) for various concentrations of cations is shown. From determinations of the readings for potassium solutions in water, replicated 6 times, the instrument error may be calculated to be

± 1 division up to readings of 50 and ± 1½ divisions thereafter.

TABLE 5.

PHOTOMETER READINGS FOR STANDARD IONIC SOLUTIONS

Readings corrected for water blank, and
corrected to 100×10^{-5} M K 100
Filters Ilford 806 + 608

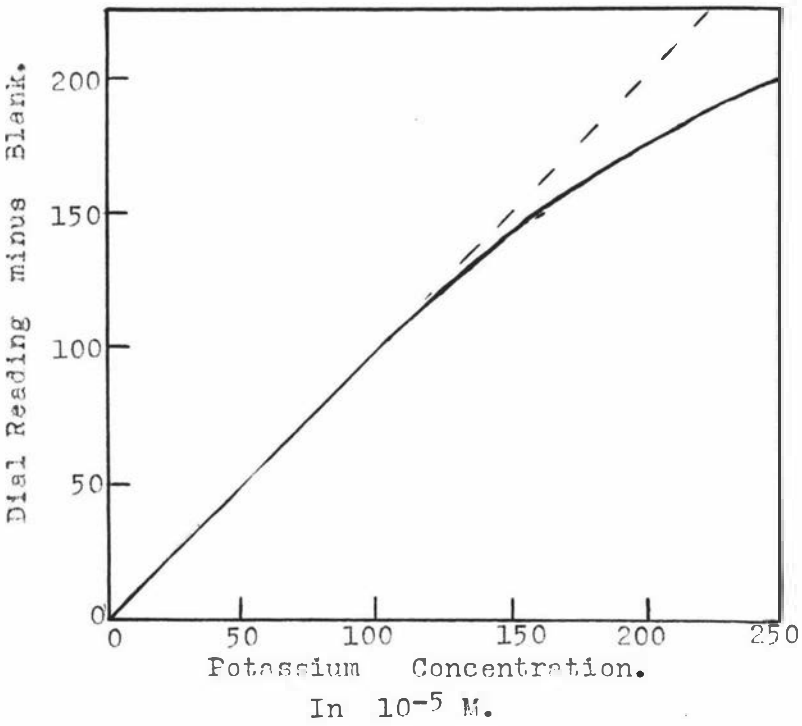
	Concentration in 10^{-5} M								
Ion	0	10	20	30	50	75	100	200	10,000
K	0	10	21	31	51	76	100	178	
NH_4							0	0	1
Ca					0		1	1	
Mg							2	3	
Ba							15	28	
Na							0		2
H							0		0

100 K plus	M/10	M
NH_4	96	93
Ca	99	
Mg	99	
Na	101	97
H	98	94
H+Ca+Mg	97	

When the filters, Ilford 806 and 608 are combined, the interference from the cations NH_4^+, Ca^{++}, Mg^{++}, Na^+ and H^+ which may be expected in some soil extracts, is seen to be unimportant. Unless barium was present in the atomised solutions, it was considered reasonable to assume that all variations in dial readings, other than from instrument drift which may be corrected by regular checking of water blank and standard potassium solutions, were caused by potassium.

From the data for photometer readings for various potassium solutions as shown in Table 5, the accompanying calibration curve was drawn for the instrument.

FIGURE 10.



Calibration curve for potassium solutions.

It is seen that for potassium concentrations up to 10^{-3} M, a linear relationship exists between potassium concentrations and dial readings but with greater concentrations, increasing extinction occurs with a marked divergence from linearity. Solutions with potassium concentrations in excess of 10^{-3} M were diluted with water to give concentrations in the range 0 - 10^{-3} M.

When ions other than potassium were present with the potassium in the atomised solutions, the apparent potassium concentration is altered slightly. In Table 5, the result of flaming solutions containing NH_4^+, Ca^{++}, Mg^{++}, Na^+ and H^+ as well as a mixture of H^+, Ca^{++} and Mg^{++} is shown. It may be seen that with additions of NH_4^+ and H^+ at M/10 and at M strengths, appreciable decreases occur in the intensity of radiation. As the solutions resulting from the soil extractions when prepared by the methods given on pages and , were approximately M/10 with respect to the hydrogen ion concentration, the standard solution of potassium was made up with N/10 HNO_3.

METHODS USED FOR THE ESTIMATION OF POTASSIUM

PLANT TISSUE

According to Dixon (Personal communication), the potassium of dried plant tissue is completely soluble in water if the tissue is boiled in water. Attoe (1948) claimed that the addition of dilute acid was necessary to ensure the complete extraction of potassium.

Trials with dried ryegrass showed that provided not more than 0.4 gm. of dried tissue, either lightly ground or whole, was heated with 200 ml. of distilled water on a boiling water bath for 30 minutes, all the potassium was extracted. Acid digestion of the extracted residue proved that all the potassium had been extracted by this treatment (Table 6).

TABLE 6.

EFFICIENCY OF BOILING WATER AS AN EXTRACTANT FOR TISSUE POTASSIUM

Weight of ground grass	Volume of water	Potassium extracted	Potassium in acid extract of residue
100 mgms.	200 ml.	4.4 mgms.	0.0 mgms.
200 mgms.	200 ml.	8.9 mgms.	0.0 mgms.
400 mgms.	200 ml.	17.6 mgms.	0.2 mgms.
400 mgms.	100 ml.	16.6 mgms.	0.9 mgms.

In practice, 0.2 gms. of high potassium grass or 0.4 gms. of low potassium grass was extracted for 1 hour with 200 ml. distilled water. The cooled aqueous extract was filtered through glass wool, made up to 250 ml. with water and flamed.

SOIL EXTRACTS

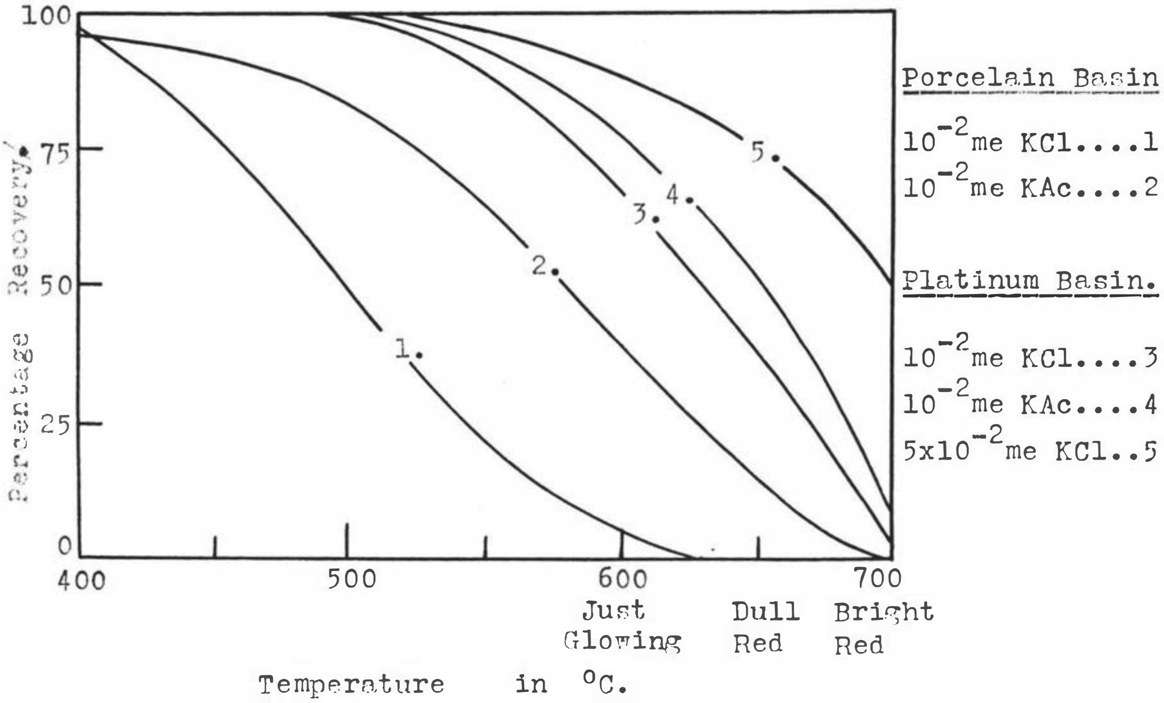
NORMAL AMMONIUM ACETATE

When flamed without prior concentration, the potassium content of the solutions from exchangeable base determinations was sometimes so low that accurate readings were not possible. If the solutions were concentrated by evaporation, the very high salt contents became troublesome, causing erratic atomizing. Ignition of the ammonium acetate extracts followed by the solution of the residue in dilute HNO_3 gave solutions which were flamed easily but which showed occasionally abnormally low potassium contents. Investigation of these extracts showed that they were associated with ignition temperatures slightly above normal (500°C) or with ignition times greater than usual (½ hour).

Published procedures for the dry ashing of plant and soil extracts recommend temperatures from 380°C (Peech, 1941) to dull red or full red heat (i.e. 600-700°C, Wright, page 256-7), for ½ hour. Peech reported that ignition of acetates at 550-600°C can lead to losses of up to 25% of the potassium present.

A close investigation of the losses of potassium on ignition, showed that appreciable losses of potassium occurred from potassium chloride on ignition in platinum basins above 450°C and from potassium acetate above 500°C. These losses increased if the heating time was prolonged. The result of heating evaporated solutions of potassium as potassium chloride or as potassium acetate at various temperatures is shown in Figure 11.

FIGURE 11.



Loss of potassium on ignition at temperatures from 400-700°C.

The recommendation of Peech (1941) is thus seen to be fully justified.

It was subsequently found that ignition of ammonium acetate extracts was unnecessary as evaporation on the waterbath left only a very small residue of ammonium salts which did not interfere with potassium radiation.

NORMAL NITRIC ACID AND OTHER ACID EXTRACTS

Although it was found possible to flame these extracts without any treatment, more reproducible results were obtained if the extracts were evaporated to dryness on the water bath. If much organic matter was present, it was destroyed by adding 6% H_2O_2 to the dried residue. After evaporation to dryness, the dried residue was then taken up in N/20 HNO_3 and if sesquioxides were present, they were precipitated with 1:1 ammonium hydroxide. Because the acid concentration at this stage was low, only a few drops of ammonium hydroxide solution was needed, giving a solution for flaming with low concentration of salts. If the sesquioxides are precipitated before the original nitric acid is evaporated, considerable amounts of ammonium hydroxide are needed and the ammonium nitrate formed is troublesome to remove.

Recovery experiments showed that virtually no potassium ($<$ 2%) was lost during the evaporation, H_2O_2 digestion and sesquioxide precipitation of the ammonium acetate and acid extracts.

METHODS FOR EXTRACTING AND FRACTIONATING SOIL POTASSIUM

EXCHANGEABLE POTASSIUM

Solutions of ammonium salts have been recommended by many workers including Schollenberger (1930) and Peech (1941) as suitable reagents for the extraction of exchangeable bases.

Normal ammonium acetate, pH 7.0, was used in the earlier part of this study to extract exchangeable potassium but it was replaced by $\underline{N}/10$ HNO_3.

1 gm. samples of soil were soaked with frequent stirring for ✓ 2 hours with 40 ml. of the extractant, followed by centrifuging, filtering and a further extraction with 40 ml. same extractant.

Comparison of the potassium extracted by the above two reagents, by $\underline{N}/5$ HNO_3, by $\underline{N}/5$ $Ba(NO_3)_2$ and by saturated $Ba(OH)_2$ showed that virtually ✓ equivalent amounts of potassium were extracted by all reagents (Table 7). With the barium solutions, sufficient H_2SO_4 was added to precipitate all the barium as $BaSO_4$. The use of $\underline{N}/10$ HNO_3 instead of $\underline{N}$ ammonium acetate is thus fully justified.

POTASSIUM EXTRACTABLE BY STRONG ACIDS

Two methods for estimating the strong acid soluble potassium were adopted viz. (a) batch extraction and (b) leaching.

BATCH EXTRACTION

The method used for the batch extraction was essentially that of Wood and DeTurk (1940). They were carried out by boiling the requisite amount of exchangeable potassium-freed soil or soil texture fraction in a 200 ml. Pyrex beaker with the appropriate amount of acid. To ensure greater accuracy in judging the boiling times with acid volumes greater than 25 ml., the acid was added boiling. After 15 minutes of boiling, the liquid was poured into 50 ml. centrifuge tubes and centrifuges at 1500-2000 rpm. for 1 minute. The supernatant liquid, which was invariably free from suspended material, was decanted carefully into 100 ml. Pyrex beakers. No attempt was made to wash the residues in the tube as the extra potassium recovered by washing was found to be less than 1% of the total for the extract.

The extracted residue was washed back into the beaker with a minimum amount of distilled water, boiling acid added and the mixture boiled for a further 15 minutes. The extractions were usually repeated to give 4 or 5

TABLE 7.

EXCHANGEABLE POTASSIUM EXTRACTED BY DIFFERENT REAGENTS

Soil	Extractant				
	N NH_4Ac pH 7.0	N/10 HNO_3	N/5 HNO_3	N/5 $Ba(NO_3)_2$	Saturated $Ba(OH)_2$
New Plymouth sandy loam	1.04	1.07	1.09	1.09	1.08
Taupo sand	0.43	0.45	0.46		
Kiripaka clay loam	1.63	1.57	1.58		
Middlehurst silt loam	0.61	0.60	0.61	0.60	0.61
Tokomaru fine sandy loam	0.60	0.58	0.61	0.60	0.60
Omakere clay loam	0.68	0.67	0.68		
Idaburn fine sandy loam	0.62	0.66	0.67	0.66	0.67
Timaru silt loam	0.31	0.30	0.30		
Halcombe silt loam	0.53	0.52	0.50		
Matamau silt loam	0.54	0.55	0.53		
Waipara silt loam	0.62	0.65	0.66		
Himatangi coarse sand	0.30	0.30	0.32		

extractions. The extracts were not bulked together but were analysed separately according to the method described on pages 40 and 41.

The weight of soil used by Wood and DeTurk (1940) was decreased by Pratt (1951) from 10 gms. to 2 gms. In this study, the weight of soil used was from 0.5 gm. to 2 gm. depending on the ratio of soil to acid. The smaller amounts of soil gave much less trouble from excessive frothing, particularly with the yellow brown pumice soils, yellow brown loams and red brown loams, and from bumping during later extractions.

LEACHING WITH ACID

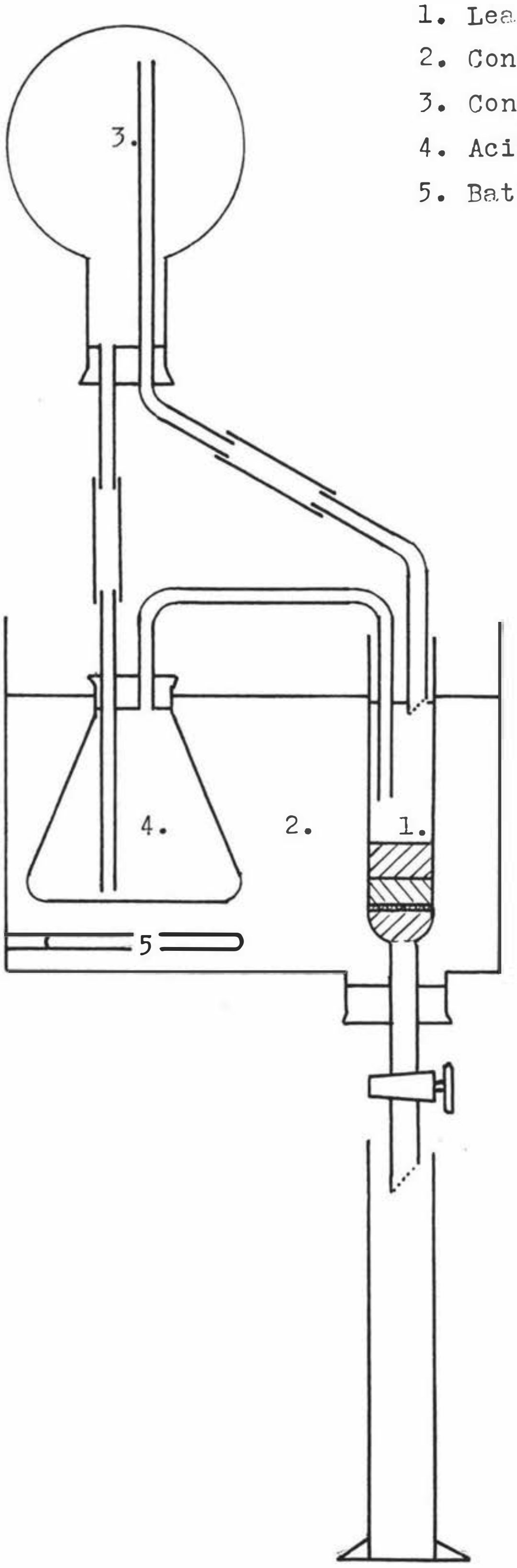
In order to observe the effect of reaction time on the amount of potassium extracted, continuous leaching of soil samples was carried out. To achieve standard conditions of leaching, an apparatus was designed incorporating the following features.

1. **Leaching Tube.** Of all glass construction, 20 cms. in length, 20 m.m. o.d. Pyrex tube, joined by an 8 mm.o.d. Pyrex tube to a Pyrex tap, which controlled the rate of flow of the extractant. The tubes used had a ground glass joint just above the level of soil in the tube but this was not essential although it facilitated the placing of the samples in the tubes.

FIGURE 12.

DIAGRAM OF LEACHING APPARATUS.

1. Leaching Tube.
2. Constant Temperature Bath.
3. Constant level acid supply.
4. Acid pre-heater.
5. Bath Heater.



DETAIL OF LEACHING TUBE.

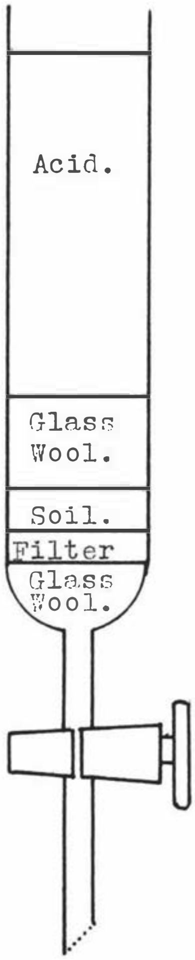


Fig. 12. - Diagram of the Leaching Apparatus and of the Leaching Tube.

The tube was mounted in a rubber stopper fitting the 1½ inch copper tubes mounted in the bottom of

2. <u>the Constant Temperature Bath.</u> This was made from unlagged sheet copper and was sufficiently large to hold 3 complete sets of leaching tubes. It was fitted with an electric 1.5 Kw heating element to maintain the water at the Boiling Point and with a constant water level device.

3. <u>A Constant Level Supply</u> incorporating a preheater for the acid leaching agent, was constructed as shown in Figure 12. For flexibility, lengths of rubber tubing were necessary in the acid feed from the reservoir to the preheater and in the air return. The stopcock in the acid feed line is required only to start and to stop the flow at the beginning and end of each leaching.

It was found that a reaction temperature of 96-97°C was maintained by this equipment at all rates of flow less than 10 ml. per minute.

Details of the apparatus are shown in Figure 12, with further details of the leaching tube showing the method of packing in a larger scale diagram in the same figure.

Liquid samples were collected at specified time intervals and the rate of leaching calculated from the observed volume of leachate. With coarse textured soils and sand fractions, no difficulty was experienced in controlling and reproducing flow rates but with fine textured soils and silt and clay fractions, flow rates were difficult to control. Because of this, the majority of the acid extractions were carried out by the batch method.

RESULTS AND DISCUSSIONS

The experimental work was carried out in the present study in 4 main sections as follows:

1. Cropping of soil samples with Italian ryegrass under intensive glasshouse conditions.
2. Extraction of the cropped soils with nitric acid to enable changes in the non-exchangeable potassium resulting from the cropping to be followed.
3. A critical examination of the conditions of extraction of potassium by nitric acid.
4. Correlation of chemically determined potassium data with the known potassium response status of soils.

In the present study, the primary object of the cropping was to reduce the available potassium level in the soils, thereby upsetting the equilibria between the forms of soil potassium. Under these conditions, it had been shown by many workers (see pages 10 et seq.) that varying amounts of non-exchangeable potassium are taken up by plants and that the soils cropped may be classified according to the amount of non-exchangeable potassium available.

Although by cropping the total uptake of available potassium may be determined, no indication of the amounts taken up of exchangeable potassium and of non-exchangeable potassium can be determined, unless chemical tests differentiating between these forms, are carried out. Extraction of the soil as a whole, although giving the above information, does not show the sources of the available potassium. To find them, it is necessary to treat fractions of the soil, e.g. the texture fractions, with the potassium extractants.

Although Olsen and Shaw (1943) and Merwin (1950) had shown by uptake measurements, that most potassium is taken up from the finer fractions, no record was found of any previous attempt to determine by chemical means which texture fractions and minerals had liberated potassium to plants.

The cropping experiment described on the following pages was designed to provide for laboratory testing, samples of soil with disturbed potassium equilibria.

UPTAKE OF POTASSIUM BY ITALIAN RYEGRASS

GROWTH IN POTS

The growth of Italian ryegrass and the potassium content of the herbage were determined at 3 weekly intervals by cutting the foliage at a height of 3 cm. from the surface of the pots and by analysing the weighed oven dried herbage as described on page 39. The individual soils differed in the amounts of dry matter produced, in the amounts of potassium taken up and in the percentage of potassium in the dried tissue.

A description of the growth characteristics of the plants grown on the 12 soils follows on pages 46 to 53.

New Plymouth Sandy Loam. Pots A3, A5, A6. Sown 2/4/53.

The grass, after striking slowly with an average of 4 seedlings per pot, grew slowly for 4 months after which it grew with increasing rapidity after October 1953, with the onset of hot weather with glasshouse air maximum temperatures up to 80-85°F, the growth rate fell rapidly. Some of the plants flowered at this time and although deflowered, almost ceased growing. In January-February 1954, many plants died and in an attempt to maintain growth, all pots of this series were resown unsuccessfully in March and successfully in May 1954. The mode of death of the plants was striking in that apparently healthy plants failed to grow after being harvested. The growth pattern in the second year was essentially similar to that of the first year with the maximum growth in October.

Initially, the potassium content of the herbage was high, 4.5-5.4% K, but it fell to 1.4-1.7% K in October 1953 and to 0.8% K in November 1953, remaining at that figure until the death of the plants in February 1954. The potassium percentage of the herbage from the resown pots was higher at 1.5% K for 2 months but it fell quickly to a constant 0.3-0.4% K when the growth rate increased in September 1954. It was noticeable that the aqueous extract of the tissues very low in potassium gave an intensely coloured sodium flame.

Potassium deficiency symptoms, e.g. marginal leaf scorch, appeared in these pots and in others when the potassium percentage in the dried tissue fell below 0.6% K.

Taupo Sand Pots C1, C2, C6. Sown 2/4/53.

The grass struck quickly with an average of 9 seedlings per pot and grew strongly until October 1953 after which growth decreased rapidly, with a high mortality rate after cuts in December 1953 and January 1954. Attempts to renew growth by reseeding were unsuccessful but seedlings transplanted in February 1955 with about 1 gm. of soil attached, grew reasonably well.

The potassium content of the herbage was from 3.7-4.0% K until September 1953 after which it fell rapidly to become 0.6% K in October 1953.

When the growth rate fell to low levels in December 1953 the potassium percentage in the herbage rose again to 1.0-1.9% K. The growth of the transplanted seedlings was low in potassium, viz. 0.7% K.

Kiripaka Clay Loam. Pots E2, E5, E6. Sown 23/4/53.

Considerable difficulty was experienced in starting growth in these pots. This very granular soil was difficult to pack around the seeds. It was also very difficult to wet and was very free draining. Young plants wilted badly until September, 1953, when sufficient roots had developed to enable them to feed from the drainage container. The plants grew strongly until early December 1953 after which growth decreased rapidly with a considerable loss of plants. The pots were replanted in May 1954 and growth during the second year followed the pattern of the first year with the maximum growth in November-December.

The potassium content of the herbage was high, 4.4-5.2% K, until November 1953, after which it fell to 1.5-2.0% K. The herbage from the replanted pots contained 2.2-3.4% K while growth was slow, but when growth became more rapid it fell to 0.3% K, with potassium deficiency symptoms appearing.

Middlehurst Silt Loam. Pots G3, G4, G5. Sown 6/5/53.

The grass seeds struck well with an average of 7 seedlings per pot and grew rapidly. These were the heaviest producing pots in September and October 1953, but growth fell off rapidly with many plants dying. All pots were resown in May 1954 but regrowth was not very vigorous.

The potassium content of the herbage was initially 3.5-5.0% K but fell to 2.2-2.5% K during the period of very rapid growth in October 1953, rising to 3.0-3.5% K and remaining at this level until the plants died in April 1954. The resown grass produced herbage with a potassium content of 3.7-5.0% K until August 1954, after which with increased growth, it fell to 1.5-1.9% K.

Tokomaru Fine Sandy Loam. Pots 12, 15, 16. Sown 26/6/53.

After a slow strike, averaging 8 seedlings per pot, the growth rate increased very rapidly until October 1953, falling off equally rapidly, all plants dying after cuts in January and February 1954. They were resown in May 1954, the pattern of growth being very similar to that of the first crop with yields of dry matter about half that of the first crop.

For the first three months, the potassium percentage in the herbage was high, viz. 4.4-5.1% K, but it fell to 0.7-1.4% K for the remainder of the first growth period. The resown grass after the initial cut contained 0.6-1.0% K.

The structure of the soil in these pots deteriorated appreciably when water was added to the surface. When the pots were resown, water was added by standing the pots in water.

Omakere Clay Loam. Pots K1, K3, K4. Sown 30/7/53.

A good strike averaging 9 seedlings per pot was followed by rapid growth until December 1953, after which growth fell off suddenly to about 1/8 of the maximum rate. The plants which had appeared quite healthy died quite suddenly after being cut in March 1954. Resowing in May 1954, was successful, reasonable growth being produced. After resowing the pots were watered as for the Tokomaru fine sandy loam pots, by standing in water.

The potassium content of the herbage fell steadily from 5.4% K in the first cut to 4.7% K in the second and to 2.1% K in the fourth cut, thereafter remaining at 1.7-2.5% K. In the second crop of grass, the potassium percentage was fairly constant throughout at 2.8-3.2% K.

Idaburn Fine Sandy Loam. Pots M1, M2, M3. Sown 12/5/54.

These pots struck well, averaging 9 seedlings per pot, and grew quite well for 4 months, after which most of the plants died. Attempts to resow and to transplant seedlings to these pots failed to give plants which lived for any length of time. This soil is virtually structureless and appears quite unsuitable for glasshouse pot trials.

The potassium content of the herbage was 3.0-3.3% K throughout.

Timaru Silt Loam. Pots N1, N2, N3. Sown 12/5/54.

After a slow start following an excellent strike averaging 11 seedlings per pot, these pots produced at a moderate rate until November 1954 after which the growth was rather poor.

The potassium content of the herbage fell from 3.0% K in September 1954 to 0.3% K in March 1955.

Halcombe Silt Loam. Pots O1, O2, O3. Sown 12/5/54.

Once established, the grass in these pots grew at a rate similar to those growing on Timaru silt loam. The greater potassium uptake was the result of a considerably higher potassium percentage in the herbage than that from the Timaru silt loam pots. The initial potassium level was 4.1% K falling slowly to 2.5% K by May 1955.

Matamau Silt Loam. Pots P1, P2, P3. Sown 17/6/54.

Seedlings transplanted at 4 per pot from pots of Timaru silt loam, struck well, making vigprous growth from August to December 1954. Considerable growth occurred until the end of the experiment in October 1955.

The potassium content of the herbage in the first cut was 3.4-4.2% K but fell to 2.0-2.4% K, 1.1-1.3% K and 0.4-0.6% K in cuts no's 2, 3 and 4. Subsequent growth contained from 0.3-0.7% K. As with the low potassium herbage from the New Plymouth sandy loam pots, these cuts had a high sodium content.

Pronounced potassium deficiency symptoms appeared during March to May 1955, but the growth rate was not depressed.

TABLE 3.

UPTAKE OF POTASSIUM AND YIELD OF DRY MATTER FROM POT TRIALS

Average of 2 months' cutting for 3 pots per soil

Soil	Soil Group	2 months ending			1953				1954					1955		
			June	August	Oct.	Dec.	Feb.	April	June	July	Sept.	Dec.	Feb.	May	August	Oct.
New Plymouth sandy loam	YB loam	mgms. K	2.8	36.5	156.0	42.2	16.5	0.0	9.7	8.7	3.1	15.6	5.1	2.9	5.7	6.0
		gms. D.M.	0.06	0.76	7.43	5.63	2.30	0.00	0.64	2.27	1.02	3.78	2.06	0.6[illegible]	1.90	2.45
		K%	4.5	4.8	2.1	0.7	0.7	- -	1.5	0.4	0.3	0.4	0.2	0.5	0.3	0.2
Taupo sand	YB pumice soil	mgms. K	7.0	62.5	58.9	10.1	0.9	-						10.0	5.0	11.1
		gms. D.M.	0.16	1.61	5.65	0.98	0.08							1.24	0.74	4.35
		K%	4.1	3.9	1.0	1.0	1.1							0.8	0.7	0.3
Kiripaka clay loam	RB loam	mgms. K	0.1	15.3	259.0	183.7	14.1	3.5	6.2	16.8	13.6	23.8	5.7	7.5	5.0	8.5
		gms. D.M.	0.00	0.35	5.92	5.21	0.73	0.20	0.21	1.28	1.17	3.74	1.83	1.27	1.01	4.10
		K%	3.3	4.4	4.4	3.5	1.9	1.7	3.0	1.3	1.2	0.6	0.3	0.6	0.5	0.2
Middlehurst silt loam	RB loam	mgms. K	2.6	70.1	191.0	61.9	25.6	9.5	29.9	7.1	4.5	11.7	15.1	16.1	20.2	27.8
		gms. D.M.	0.04	1.78	7.70	2.36	0.78	0.29	0.74	0.42	0.29	0.54	0.93	0.60	0.87	1.66
		K%	6.5	3.9	2.5	2.3	3.3	3.3	4.0	1.7	1.6	2.1	1.6	2.7	2.3	1.7
Tokomaru fine sandy loam	YGE	mgms. K	-	13.7	149.4	33.9	11.7	0.0	1.4	9.5	8.5	15.4	4.3	2.5	10.7	17.7
		gms. D.M.	-	0.28	5.47	2.99	0.71	0.0	0.05	1.22	1.21	1.82	1.39	0.42	0.79	1.86
		K%		4.9	2.5	1.1	1.6	-	2.8	0.8	0.7	0.7	0.3	0.6	1.3	0.9
Omakere clay loam	YGE	mgms. K	-	1.3	155.8	98.0	14.9	0.0	24.1	23.1	13.7	24.0	4.1	27.5	16.2	23.0
		gms. D.M.	-	0.02	4.91	4.24	0.87	0.0	0.65	0.82	0.61	1.04	1.24	0.98	0.74	1.35
		K%		6.5	3.2	2.3	1.7	-	3.7	2.8	2.2	2.4	0.3	2.9	2.2	1.7

TABLE 9.

CUMMULATIVE UPTAKE OF POTASSIUM AND CUMMULATIVE YIELD OF DRY MATTER FROM POT TRIALS

Average for 3 pots per soil

Soil	Soil Group	Period ending	1953 June	August	Oct.	Dec.	Feb.	1954 April	June	July	Sept.	Dec.	Feb.	1955 May	August	Oct.
New Plymouth sandy loam	YB loam	mgms. K	2.3	39.3	195.3	237.5	254.0	254.0	263.7	272.4	275.5	291.1	296.2	299.1	304.8	310.8
		gms. D.M.	0.06	0.82	8.25	13.88	16.18	16.18	16.62	19.09	20.11	23.89	25.95	26.55	28.45	30.80
Taupo sand	YB pumice soil	mgms. K	7.0	69.5	128.4	138.5	139.4							149.4	154.4	165.5
		gms. D.M.	0.16	1.77	7.42	8.40	8.48							9.72	10.46	14.81
Kiripaka clay loam	RB loam	mgms. K	0.1	15.4	274.4	458.1	472.2	475.7	481.9	498.7	512.3	536.1	541.8	535.5	540.5	549.0
		gms. D.M.	0.00	0.35	6.27	11.48	12.21	12.41	12.62	13.90	15.07	18.81	20.64	21.62	22.63	26.73
Middlehurst silt loam	RB loam	mgms. K	2.6	72.7	303.7	335.6	361.2	370.7	400.6	407.7	412.2	423.9	439.0	479.8	500.0	527.8
		gms. D.M.	0.04	1.82	9.52	11.88	12.66	12.95	13.69	14.11	14.40	14.94	15.87	17.19	18.08	19.72
Tokomaru fine sandy loam	YGE	mgms. K	-	13.7	183.1	197.0	208.7	208.7	210.1	219.6	228.1	241.5	245.8	248.3	259.0	276.7
		gms. D.M.	-	0.28	6.75	9.74	10.45	10.45	10.50	11.78	12.99	14.81	16.20	16.62	17.41	19.27
Omakere clay loam	YBE	mgms. K	-	1.3	157.1	255.1	270.0	270.0	294.1	317.2	330.9	354.9	359.0	386.5	402.7	415.7
		gms. D.M.	-	0.02	4.93	9.17	10.04	10.04	10.69	11.51	12.12	13.16	14.40	15.36	16.10	17.45

TABLE 10

UPTAKE OF POTASSIUM AND YIELD OF DRY MATTER FROM POT TRIALS

Average of 2 months' cutting for 3 pots per soil

Soil	Soil Group	2 months ending	1954 July	1954 Sept.	1954 Nov.	1955 Jan.	1955 March	1955 May	1955 August	1955 Oct.
Idaburn fine sandy loam	BGE	mgms. K	2.2	44.8	10.0	4.8	7.8	3.8	10.2	21.6
		gms. D.M.	0.07	1.36	0.30	0.13	0.22	0.13	0.31	0.86
		K %	3.1	3.3	3.3	3.6	3.5	3.0	3.3	2.5
Timaru silt loam	YGE	mgms. K	1.9	59.5	64.7	9.7	4.0	2.2	14.3	23.2
		gms. D.M.	0.05	2.08	2.86	0.68	0.63	0.09	0.82	1.81
		K %	3.8	2.9	2.3	1.4	0.7	2.4	1.8	1.3
Halcombe silt loam	YGE	mgms. K	0.5	22.0	103.0	16.6	8.9	13.0	15.6	26.8
		gms. D.M.	0.02	0.53	3.16	0.45	0.38	0.55	0.80	1.39
		K %	2.5	4.1	3.3	3.7	2.4	2.4	1.9	1.9
Matamau silt loam	YB loam	mgms. K	2.0	110.8	62.7	10.7	4.8	2.6	3.0	3.2
		gms. D.M.	0.06	5.10	8.19	2.07	0.82	0.62	0.92	1.11
		K %	3.3	2.2	0.8	0.5	0.6	0.4	0.3	0.3
Waipara silt loam	YGE	mgms. K	-	118.8	129.1	40.3	12.3	14.8	23.5	25.5
		gms. D.M.	-	3.36	5.12	1.68	0.50	0.76	1.56	1.64
		K %		3.6	2.5	2.4	2.5	2.0	1.5	1.5
Himatangi coarse sand	YB sand	mgms. K	-	58.8	55.4	13.8	0.8	5.1	4.0	8.6
		gms. D.M.	-	3.48	4.38	1.58	0.08	0.58	0.43	1.87
		K %		1.7	1.3	0.8	1.0	0.9	0.9	0.5

TABLE 11

CUMULATIVE UPTAKE OF POTASSIUM AND CUMULATIVE YIELD OF DRY MATTER FROM POT TRIALS

Average of 3 pots per soil

Soil	Soil Group	Period ending	1954 July	Sept.	Nov.	1955 Jan.	March	May	August	Oct.
Idaburn fine sandy	BGE loam	mgms. K	2.2	47.0	57.0	61.8	69.6	73.4	83.6	105.2
		gms. D.M.	0.07	1.43	1.73	1.86	2.08	2.21	2.52	3.38
Timaru silt loam	YGE	mgms. K	1.9	61.4	126.1	133.8	139.8	142.0	156.3	179.5
		gms. D.M.	0.05	2.13	4.90	5.67	6.20	6.29	7.11	8.92
Halcombe silt loam	YGE	mgms. K	0.5	22.5	125.5	142.1	151.0	164.0	179.6	206.4
		gms. D.M.	0.02	0.55	3.71	4.16	4.54	5.09	5.89	7.23
Matamata silt loam	YB loam	mgms. K	2.0	112.8	175.5	186.2	191.0	193.6	196.6	199.8
		gms. D.M.	0.06	5.16	13.35	13.62	16.44	17.06	17.98	19.09
Waipara silt loam	YGE	mgms. K	-	113.8	247.9	298.2	300.5	315.3	328.8	364.3
		gms. D.M.	-	3.36	8.48	10.16	10.66	11.42	11.98	13.62
Himatangi coarse sand	YB sand	mgms. K	-	58.8	114.2	128.0	128.8	133.9	137.9	146.5
		gms. D.M.	-	3.48	7.86	9.44	9.52	10.10	10.53	12.40

Waipara Silt Loam. Pots Q1, Q2, Q3. Sown 28/7/54.

Seedlings grown in Taupo sand for one month were transplanted at 4 per pot and immediately made vigorous growth. The growth rate declined in January 1955 to about one quarter of the maximum rate.

The initial cut of herbage contained 3.5% K but subsequent cuts contained from 2.1-2.6% K.

Himatangi Coarse Sand. Pots R1, R2, R3. Sown 28/7/54.

Seedlings grown in Taupo sand for one month and transplanted at 4 per pot grew at a rate very similar to that of seedlings planted in Waipara silt loam, except for the month of February 1955, when the plants in the Himatangi sand produced very little foliage.

The potassium content of the herbage was low throughout starting at 1.6-1.9% K, falling to 0.9% K by January 1955 and remaining at this figure until October 1955 when it fell to 0.5% K, plants then showing potassium deficiency symptoms.

The amount of potassium taken up by the ryegrass and the amount of dry matter produced during the period of cropping is shown in detail in Tables 8, 9, 10, 11.

EXCHANGEABLE POTASSIUM LEVELS

During the period of cropping, the level of exchangeable potassium in the pots was determined at intervals of approximately 6 months. The "initial" sampling date mentioned in most tables of results referring to cropped soils is the date of sowing of the pots, and the data under this heading refer to that determined on uncropped, unfertilized laboratory samples specified on page 27. Table 12 sets out the "initial" sampling dates, i.e. the dates of sowing of the pots.

TABLE 12

INITIAL SAMPLING DATES, i.e. DATES OF SOWING

Soil	Date
New Plymouth sandy loam	2.4.53.
Taupo sand	2.4.53.
Kiripaka clay loam	23.4.53.
Middlehurst silt loam	6.5.53.
Tokomaru fine sandy loam	26.6.53.
Omakere clay loam	30.7.53.
Idaburn fine sandy loam	12.5.54.
Timaru silt loam	12.5.54.
Halcombe silt loam	12.5.54.
Matamau silt loam	17.6.54.
Waipara silt loam	28.7.54.
Himatangi coarse sand	28.7.54.

ch 4

These determinations, reported in Table 13, show that the level of exchangeable potassium in the bulk soil samples, collected in all cases during periods of slow growth, fell, to a more or less constant level when these soils were subjected to more intensive growth under glass-house conditions. The attaining of this constant minimum level of exchangeable potassium coincided with the reaching of a minimum level of potassium in the ryegrass.

TABLE 13

EXCHANGEABLE POTASSIUM IN POT SOILS

Samples oven dried before analysis

Soil	Sampling dates: Initial	29.10.53.	8.3.54.	28.9.54.	13.12.54.	29.3.55.	10.8.55.	15.10.55.
	me%	me%	me%	me%	me%	me%	me%	me%
New Plymouth sandy loam	1.10	0.45	0.26	0.20	0.16	0.18	0.20	0.20
Taupo sand	0.46	0.15	0.11	0.12	0.14	0.14	0.12	0.10
Kiripaka clay loam	1.56	0.80	0.24	0.20	0.16	0.16	0.16	0.20
Middlehurst silt loam ((2mm)	0.61	0.33	0.35	0.34	0.35	0.45	0.48	0.49
Tokomaru f.s. loam	0.61	0.22	0.17	0.13	0.10	0.12	0.12	0.14
Omakere clay loam	0.68	0.30	0.24	0.22	0.20	0.22	0.30	0.31
Idaburn f.s. loam	0.65	-	-	0.54	0.49	0.55	0.56	0.48
Timaru silt loam	0.30	-	-	0.23	0.16	0.28	0.30	0.26
Halcombe silt loam	0.52	-	-	0.50	0.18	0.25	0.29	0.18
Matamau silt loam	0.55	-	-	0.30	0.22	0.26	0.26	0.22
Waipara silt loam	0.85	-	-	0.47	0.30	0.42	0.47	0.40
Himatangi coarse sand	0.30	-	-	0.20	0.16	0.16	0.16	0.14

In general, the exchangeable potassium level of the pots was reflected in the proportion of potassium in the dry matter, particularly where there was little release of nonexchangeable potassium. Exact relationships between the exchangeable potassium and the percentage of potassium in the dry matter would not be expected

a. Because of variations in the growth rate brought about by environmental conditions not related to the potassium content, e.g. the depressing effects on growth of soil temperatures in excess of 70°F on ryegrass growth (Mitchell, 1955).

b. Because of variations in the ability of the soils to supply sodium which is able to replace in part the potassium needed by plants. ✓

c. Because of increasing maturity of the plants. Wells (1954) has shown that the potassium percentage of sweet vernal decreases considerably with increasing maturity. Italian ryegrass would probably react similarly.

A comparison of the total uptake of potassium by the ryegrass on the basis of 1000 gms. of oven dry soil per pot (Table 14) and the exchangeable potassium levels during the cropping period (Table 13) shows that potassium which was not exchangeable at the beginning of the cropping was taken up by the ryegrass plants. The amounts of nonexchangeable potassium taken up are given in Table 15, the data for which was calculated by subtracting the initial exchangeable potassium values from the sum of the residual exchangeable potassium and the potassium removed by cropping.

It may be seen that considerable amounts of nonexchangeable potassium, up to 1.76 me% K, were used. There appears to be no correlation between the uptake of nonexchangeable potassium and the initial exchangeable potassium level (Figure 13), but the uptake of nonexchangeable potassium and the residual exchangeable potassium level appears to be related (Figure 14).

FIGURE 13.

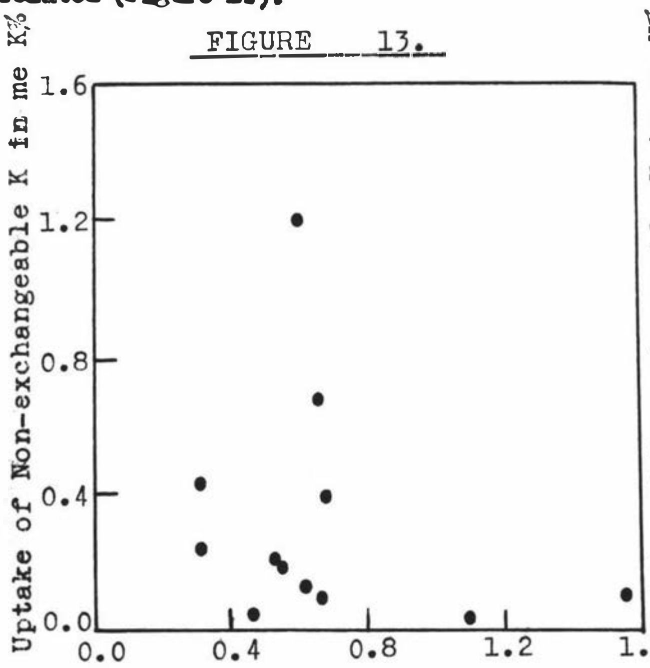


Fig.13.- Relationship between uptake of non-exchangeable Potassium and initial exchangeable Potassium. 15 months cropping.

FIGURE 14.

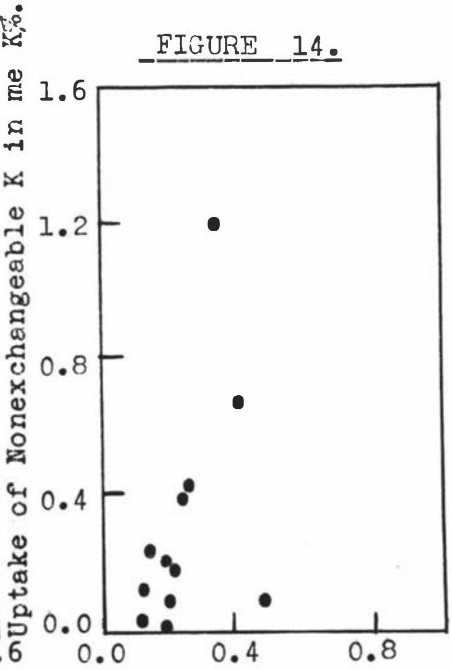


Fig.14.- Relationship between uptake of non-exchangeable Potassium and residual exchangeable Potassium. 15 months cropping.

Because of the main object of the pot trials was to observe the effects of plant growth on the forms of soil potassium, no attempt was made to ensure that maximum growth took place but rather that a reasonable growth rate was maintained. For this reason and because there were only 3 replicates for each soil, the yields of dry matter and the potassium uptake must not be regarded as an exact measure of potassium availability to be used for comparing one soil with another.

TABLE 14

CUMULATIVE UPTAKE OF POTASSIUM

All values expressed in me.K %. calculated on the basis of 1000 gms. oven dry soil per pot

Soil / Sampling dates	29.10.53.	8.3.54.	28.9.54.	15.12.54.	29.3.55.	10.8.55.	15.10.55.
	me%	me%	me%	me%	me%	me%	me%
New Plymouth sandy loam	0.61	0.79	0.86	0.91	0.94	0.96	0.98
Taupo sand	0.34	0.36	0.36	0.36	0.36	0.39	0.42
Kiripaka clay loam	0.78	1.34	1.47	1.53	1.54	1.55	1.57
Middlehurst silt loam	0.71	0.98	1.12	1.15	1.18	1.36	1.43
(< 2 mm.)	0.93	1.28	1.46	1.50	1.56	1.78	1.88
Tokomaru f.s. loam	0.43	0.56	0.61	0.65	0.67	0.70	0.74
Omakere clay loam	0.40	0.69	0.85	0.91	1.00	1.04	1.07
Idaburn f.s. loam	-	-	0.12	0.16	0.17	0.20	0.26
Timaru silt loam	-	-	0.16	0.35	0.36	0.40	0.46
Halcombe silt loam	-	-	0.06	0.36	0.39	0.46	0.53
Matamau silt loam	-	-	0.29	0.48	0.49	0.51	0.51
Waipara silt loam	-	-	0.30	0.74	0.77	0.84	0.93
Himatangi coarse sand	-	-	0.15	0.33	0.33	0.35	0.37

TABLE 15

UPTAKE OF POTASSIUM FROM NONEXCHANGEABLE SOURCES

Soil / Sampling date	29.10.53.	8. 5.54.	28. 9.54.	15.12.54.	29. 5.55.	10. 8.55.	15.10.55.
	me%	me%	me%	me%	me%	me%	me%
New Plymouth sandy loam	-0.04	-0.05	-0.04	-0.03	0.01	0.06	0.08
Taupo sand	0.03	0.01	0.02	0.04	0.04	0.05	0.06
Kiripaka clay loam	0.02	0.02	0.11	0.13	0.14	0.15	0.21
Middlehurst silt loam (<2mm.)	0.65	1.02	1.19	1.22	1.38	1.65	1.76
Tokomaru f.s. loam	0.04	0.12	0.13	0.15	0.18	0.21	0.27
Omakere clay loam	0.02	0.25	0.39	0.45	0.54	0.66	0.70
Idaburn f.s. loam			0.01	0.00	0.07	0.11	0.09
Timaru silt loam			0.09	0.21	0.34	0.40	0.42
Halcombe silt loam			0.04	0.02	0.12	0.25	0.19
Matamau silt loam			0.04	0.15	0.20	0.22	0.18
Waipara silt loam			0.12	0.39	0.54	0.66	0.68
Himatangi coarse sand			0.05	0.19	0.19	0.21	0.21

NITRIC ACID EXTRACTIONS

As it was considered that exchangeable potassium figures would not give sufficient information with regard to the potassium status of the soil, it was decided, on the basis of published work, to investigate the soils used for cropping by extracting with N HNO_3.

Although the majority of workers had adopted a single 10 minute boiling after a preliminary 15 minute soaking at room temperature, at a soil to acid ratio of 1 gm. soil to 10 ml N acid or at 1 gm. to 12½ ml N acid because of the excellent correlations between crop yields and the acid soluble potassium values so determined, there were reports that the amount of potassium was dependent on the conditions of extraction. For example, DeTurk, Wood and Bray (1943) found that over the range N - 10 N acid, the amount of potassium extracted, increased with the strength of acid up to 5 N. Reitemeier et al (1951) showed a marked increase in potassium extracted by 5 N HNO_3 and 60% $HClO_4$ compared with N acids and Rouse and Bertramson (1949) stated that the amount of potassium extracted by acid increased with increasing time of extraction and with increasing soil to acid ratio over an undefined range.

To test the above reports of the effects of time of heating and of variations in acid concentration and to find whether a different boiling time was more suitable, 5 gm. samples of 3 soils, previously freed from exchangeable bases by soaking for 2 hours and one hour in N/10 HNO_3, were extracted with 500ml. N HNO_3, added boiling, and maintained boiling for one hour. 25 ml. samples of the extracting liquid were taken immediately (i.e. within 1 minute) and after boiling for 5, 10, 15, 20, 30 and 60 minutes.

TABLE 16

THE EFFECT OF THE TIME OF HEATING ON POTASSIUM SOLUBLE IN N HNO_3.

Ratio of soil to acid 1 gm.: 100 ml.
Sample weight 5 gms.
Duplicate determinations reported.

	Time of sampling in minutes						
Soil	1	5	10	15	20	30	60
	me%	me%	me%	me%	me%	me%	me%
Middlehurst	0.24	1.93	3.53	4.32	4.60	4.90	5.54
silt loam	0.14	1.71	3.82	4.37	4.63	4.88	5.48
Tokomaru	0.10	0.36	0.60	0.89	1.05	1.43	2.20
fine sandy loam	0.12	0.41	0.64	0.87	1.03	1.40	2.18
New Plymouth	0.02	0.12	0.21	0.31	0.39	0.56	1.06
sandy loam	0.00	0.13	0.22	0.31	0.38	0.58	1.07

In this and in other extractions, when the volume of acid exceeded 25 ml., it was found that several minutes were required to raise the temperature of the liquid to the boiling point, e.g. 100 ml. requiring about 4-5 minutes. It was easier to reproduce accurately the boiling times if the acid was boiling when added to the soil. When this was done, only

20-30 seconds were required to bring the mixture back to the boiling point, irrespective of the volume added.

The results of the above extraction, (Table 16) show that the amount of potassium extracted, increased with the time of heating for all the soils tested, the rate of increase varying between the soils. By doubling the time of extraction from 10 to 20 minutes or from 15 to 30 minutes or from 30 to 60 minutes, the amount of potassium extracted from the New Plymouth sandy loam was nearly doubled but for the Tokomaru fine sandy loam, the increase was only 50% and for the Middlehurst silt loam, the increase was 15-20% after the first 10 minutes, during which time, the potassium extracted increased very rapidly. The variation between duplicate extractions was found to be larger with the 5 minute and 10 minute extractions than with the 15 minute and longer extractions. The extraction time of 10 minutes recommended and used by other workers was therefore amended to one of 15 minutes.

In the course of boiling a soil sample with $\underline{N}$ HNO_3, oxidation of the organic matter occurs with the evolution of carbon dioxide. With soils high in organic matter, such as the New Plymouth sandy loam, this carbon dioxide produces large amounts of froth. It is necessary, therefore, to use wide mouthed vessels, such as beakers, for the extractions with the consequent risk of volume changes during the extractions.

The effect of varying the concentration of acid, while keeping the total amount of acid constant, was checked for the Middlehurst silt loam, Tokomaru fine sandy loam and New Plymouth sandy loam. Table 17 shows that provided the acid concentrations are kept between $\underline{N}/2$ and 2 $\underline{N}$, no error should be caused by varying acid concentrations. Thus it was possible to neglect small changes in the volume of the extracting liquid brought about by evaporation of water during extractions. Further, the presence of small amounts of water from the washing back of the soil residues from the centrifuge tubes after the separation of the extracting solutions and soil residues, should cause no error in the estimations.

TABLE 17

THE EFFECT OF ACID CONCENTRATION ON POTASSIUM SOLUBLE IN NITRIC ACID

Ratio of soil to acid 1 gm.: 100 me. acid.
Time of heating 15 minutes.

Soil	Acid concentration.				
	N/4 me%	N/2 me%	N me%	2 N me%	4 N me%
Middlehurst silt loam	3.54	4.26	4.35	4.35	4.62
Tokomaru fine sandy loam	0.69	0.88	0.86	0.90	0.98
New Plymouth sandy loam	0.26	0.31	0.31	0.32	0.35

CONTINUOUS LEACHING WITH HOT NITRIC ACID

To check further on the effects of varying the time of extraction and the acid concentration, samples of soils and their texture fractions were leached with hot acid at varying flow rates, over a range of acid strengths, in the apparatus described on pages 42, 43 & 44.

The exchangeable potassium was extracted from 2 gm. samples of soil by twice soaking for 2 hours with 40 ml. neutral N ammonium acetate. The exchangeable potassium freed soil was washed with distilled water to remove excess ammonium acetate and transferred wet to the leaching tubes. Boiling N HNO_3 was added to the tubes, the constant acid level device fitted and the leaching started, samples being taken at predetermined intervals, usually after 5 minutes and then at 10 or 15 minutes intervals.

Analysis of the extracts showed that virtually no potassium was leached during the first 5 minutes and except for the Middlehurst silt loam, after 15 minutes leaching, potassium was extracted at a nearly constant rate. The Middlehurst silt loam yielded considerable amounts of potassium for 45 minutes after which it yielded much less potassium at an approximately constant rate (Figure 15).

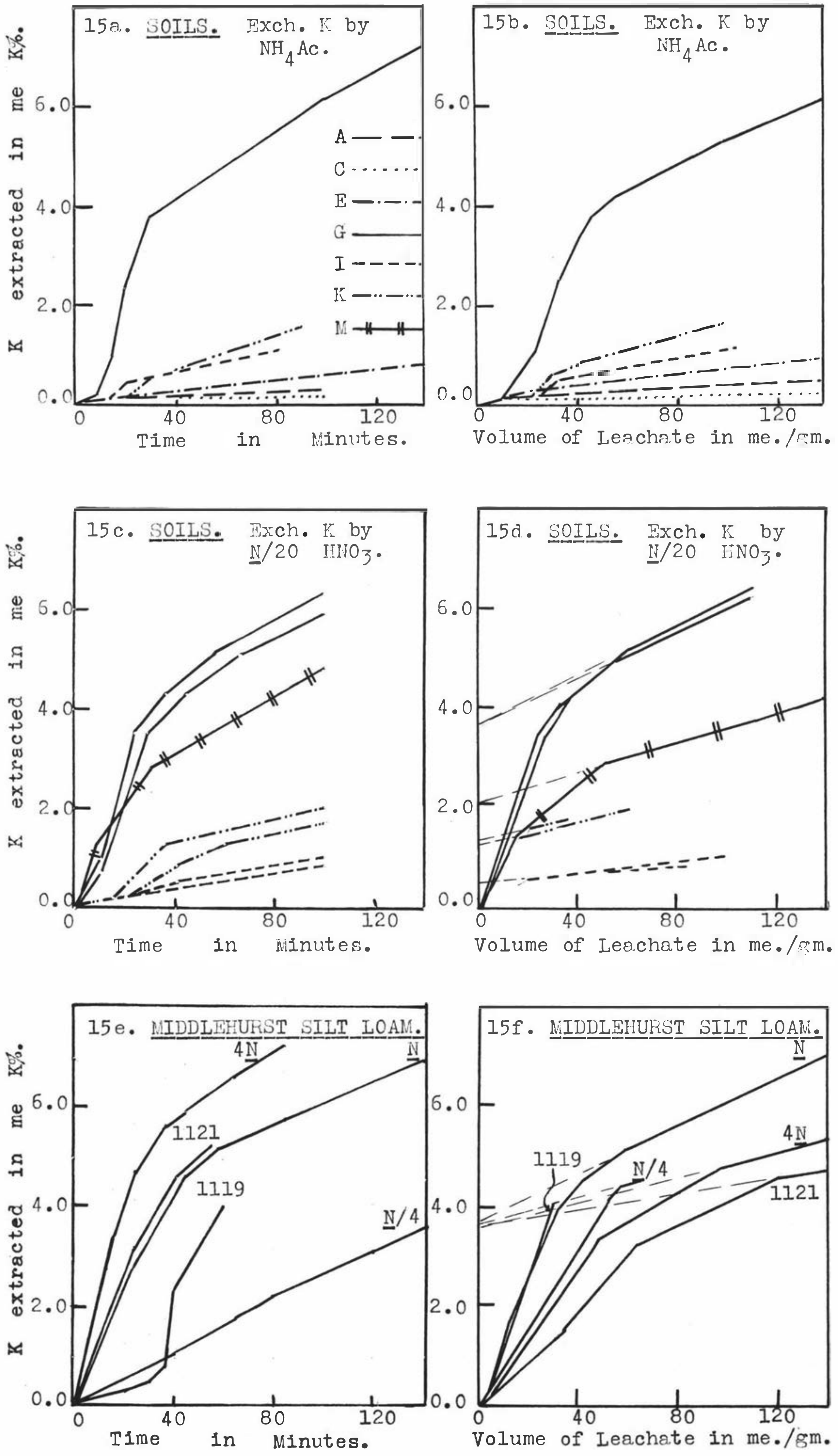
When the exchangeable potassium was removed before leaching, by dilute HNO_3 instead of by ammonium acetate, appreciable amounts of potassium were extracted during the first 5 minutes. From the Middlehurst silt loam and from the Omakere clay loam, potassium was extracted faster in the initial stages of leaching than when ammonium acetate was used to remove the exchangeable cations, (Figure 15).

During these extractions, different flow rates, probably caused by variations in the packing of the soil in the tubes, persisted throughout the duplicate extractions of the Tokomaru fine sandy loam and the Omakere clay loam. In both cases, the slower leaching rates brought out less potassium in a given time than did faster leaching (Figure 15). To check whether the variations were brought about by the differences in leaching rates, 2 samples of the Middlehurst silt loam were leached at different flow rates. At the flow rates tested, nearly identical amounts of potassium were extracted by any given volume of acid with a tendency for the slower extractions to extract slightly more potassium per unit of volume at the end of the extractions than the faster ones. This shows as a slight divergence between the curves formed when the potassium extracted is plotted against the volume of extract (Figure 15).

A more thorough examination of the behaviour of the Middlehurst silt loam when subjected to varying leaching rates revealed that at flow rates less than 5 ml. N acid per minute, the amount of potassium extracted was governed entirely by the volume of leachate (Figure 15 e,f). Without preheating of the acid, flow rates above 2 ml. acid per minute extracted less potassium in a given volume than did slower rates. At flow rates of 4 ml. per

FIGURE 15.

NON-EXCHANGEABLE POTASSIUM EXTRACTED BY LEACHING WITH HNO_3.



minute, without preheating the reagent temperature was 92°C, with preheating 97°C and it is considered that this difference in temperatures would produce the difference between extraction figures found at higher flow rates with and without preheating.

With acid concentrations other than N, some divergence was found at N/4 and at 4 N but with N/2 and 2 N solutions, the amounts of potassium extracted for any given amount of acid expressed as milliequivalents of acid per gm. soil were the same as for N acid. As with batch extractions, N/4 acid extracted less potassium than stronger acids in equivalent amounts of acid. 4 N acid, although extracting more potassium than N acid at the same volume flow rate, under the conditions of the extraction tested, i.e. a flow rate equivalent to 8 ml. N HNO_3 /gm. soil/minute, (actual flow rate 2 ml. 4 N HNO_3 per minute), did not extract as much potassium per equivalent amount of acid as did N HNO_3 at 2 ml/min. At slower rates, it is probable that the 4 N HNO_3 would have extracted as much if not more potassium than the N HNO_3.

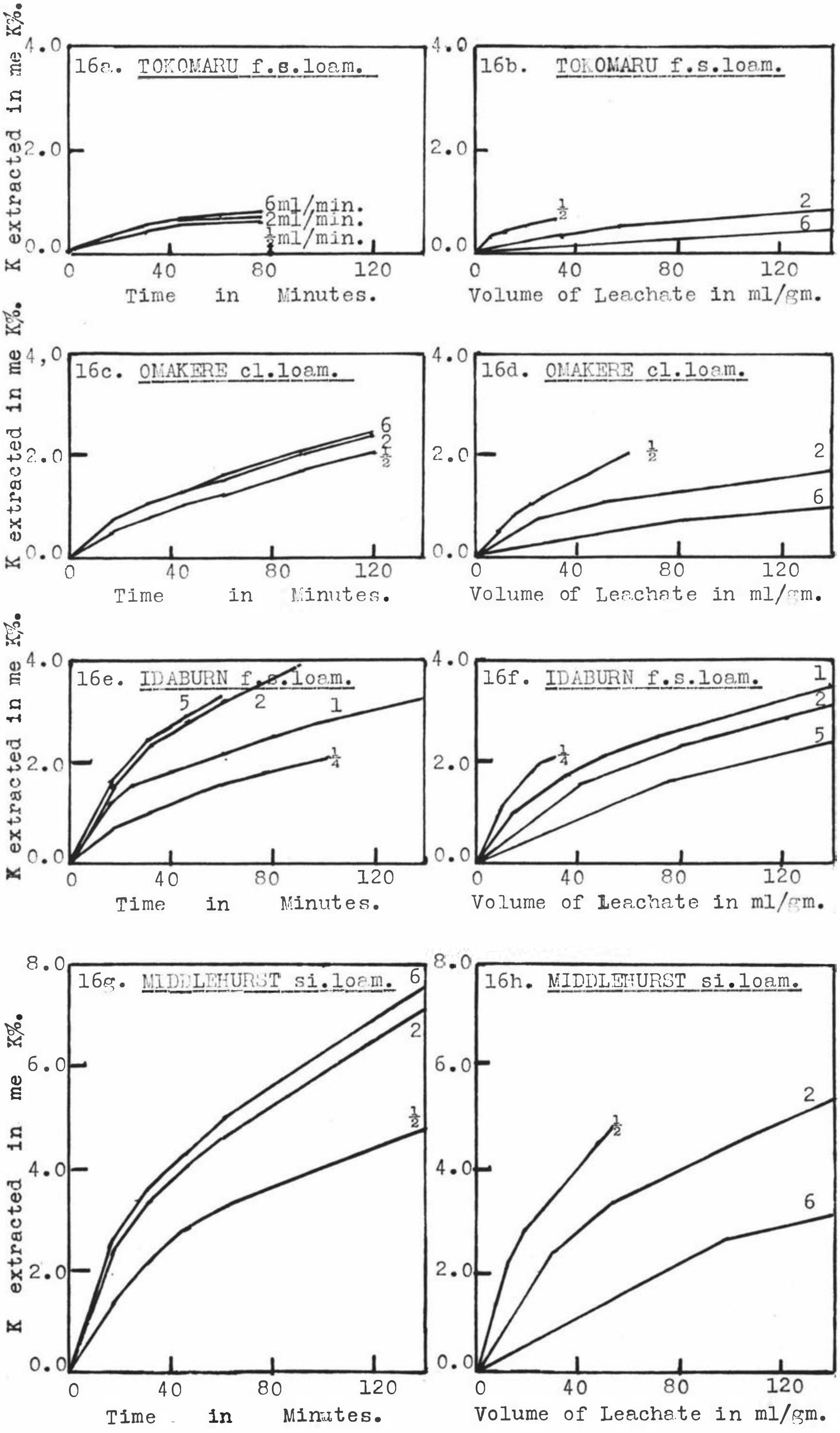
It appears that there is a minimum amount of acid required to ✓ leach out any given amount of potassium. There also appears to be a maximum rate of reaction between the acid and the soil (compare extraction No. 1121 with other extractions with N HNO_3 Figure 15 e,f). The close dependence of the potassium extracted on the volume of extractant at slow leaching rates could imply that a solution saturated with regard to some reaction, product, was formed. When the leaching was fast, the observed divergences may have been caused by incomplete reaction with the rapidly flowing acid or by more acid being added than the soil could react with.

When 1 gm. samples of fine sand (not deferrated) separated by Method B (page 27) from Middlehurst silt loam, Tokomaru fine sandy loam, Omakere clay loam and Idaburn fine sandy loam, were extracted at approximately 1/2, 2 and 6 ml. N HNO_3 per minute, (Figure 16), in no case was there good agreement between the potassium extracted and the volume of extractant, indicating that the two faster flow rates at least, were in excess of that required to produce the maximum rate of reaction. The close agreement between the amounts of potassium extracted and the time of extraction for the two faster rates lends support to this suggestion.

✓ Although a comparison of extractions of soils leached at flow rates sufficiently slow to enable the minimum amount of acid to leach out the maximum amount of potassium is possible in theory, in practice, this would require several determinations to ensure that the rates were not so fast that the acid was unable to react fully with the soil. A sounder procedure would be to leach at the maximum rate possible and to compare the maximum rates of reaction. Difficulty is experienced with soils high in silt or in clay in carrying this out because of the limited rate of percolation of acid

FIGURE 16.

NON-EXCHANGEABLE POTASSIUM EXTRACTED FROM FINE SANDS BY LEACHING WITH NORMAL NITRIC ACID.



through these soils. It is probable that improved rates of percolation could be achieved by mixing quartz sand with such soils or by increasing the bore of the leaching tubes to give thinner discs of soil. Alternatively, increasing the concentration of the acid to 4 N or higher would increase the equivalents of acid leached.

BATCH EXTRACTION WITH NITRIC ACID

An alternative approach tried in order to find the maximum rate of reaction between the soil and the acid, was to vary the ratio of soil to acid in the 15 minute boiling method. The "batch" extraction method, was so called to distinguish it from the continuous leaching method, over which it possesses several advantages viz.

1. Exact control of the soil to acid ratio.
2. The ease of leaching of the acid through the disc of soil or texture fraction, which limits the range of extraction conditions with continuous leaching, does not affect batch extraction.
3. A much wider range of soil to acid ratios, e.g. 1:1,000, is possible with batch extraction.

Samples of the 12 soils used in the long term cropping experiment were extracted at ratios of soil to acid, expressed as grams of oven dry soil per ml. N acid, of $1:12\frac{1}{2}$, 1:100 and 1:200. In all cases except where otherwise stated, the exchangeable potassium was removed prior to digestion with N HNO_3 by soaking for 2 hours with 40 ml. N/10 HNO_3 followed by a second soaking for one hour with 40 ml. N/10 HNO_3. The soils, New Plymouth sandy loam, Taupo sand, Kiripaka clay loam, Middlehurst silt loam, Tokomaru fine sandy loam and Omakere clay loam were also extracted at a soil to acid ratio of $1:12\frac{1}{2}$ after removal of exchangeable potassium with neutral N ammonium acetate. The results of these extractions are reported in Table 18.

At the soil to acid ratio of $1:12\frac{1}{2}$, the first extraction following the removal of exchangeable potassium with ammonium acetate was very much smaller than that where N/10 HNO_3 was used to remove the exchangeable potassium, for the Middlehurst silt loam, Tokomaru fine sandy loam and Omakere clay loam. For the other three soils there was no difference. In subsequent extractions of the Tokomaru fine sandy loam and Omakere clay loam, there was little difference between the ammonium treated soil and the hydrogen treated soil. With the Middlehurst silt loam, differences persisted until the fifth extraction.

Although there were considerable differences between the amounts of potassium extracted by the N HNO_3 from the various soils, the pattern of each extraction was similar. Where N/10 HNO_3 was used to remove exchangeable potassium, the first N HNO_3 treatment extracted the most potassium, with a nearly constant amount of potassium in each extract after the second. The Middlehurst silt loam showed a decline in the potassium content of the extracts up to the fifth extract.

TABLE 18

POTASSIUM SOLUBLE IN NORMAL NITRIC ACID

Time of Heating 15 minutes.

Exchangeable potassium removed before extractions with N/10 HNO_3 except analyses marked * , where N ammonium acetate, pH 7 used.

Soil		Ratio	Exch. K	Extraction Number 1	2	3	4	5	"Step" K	"Constant" rate K
			me%	me%	me%	me%	me%	me%	me%	me%
New Plymouth	*	1:12½	1.04	0.26	0.14	0.16	0.16	0.18	0.1	0.16
sandy loam		1:12½	1.09	0.24	0.21	0.20	0.20	0.19	0.05	0.20
		1:100	1.10	0.31	0.25	0.26	0.25	0.25	0.05	0.25
		1:200	1.12	0.30	0.25	0.24	0.26	0.26	0.05	0.25
Taupo	*	1:12½	0.43	0.22	0.08	0.09	0.07	0.08	0.1	0.07
sand		1:12½	0.46	0.20	0.12	0.09	0.09	0.09	0.1	0.09
		1:100	0.45	0.32	0.18	0.16	0.15	0.14	0.2	0.15
		1:200	0.46	0.40	0.20	0.21	0.23	0.22	0.2	0.22
Kiripaka	*	1:12½	1.63	0.18	0.07	0.09	0.07	0.06	0.1	0.06
clay loam		1:12½	1.54	0.29	0.15	0.14	0.14	0.15	0.1	0.15
		1:100	1.57	0.37	0.22	0.18	0.17	0.19	0.2	0.18
		1:200	1.57	0.41	0.25	0.23	0.21	0.22	0.2	0.22
Middlehurst	*	1:12½	0.61	1.51	2.05	1.04	0.69	0.54	3.1	0.55
silt loam		1:12½	0.65	3.00	1.46	0.75	0.60	0.49	3.8	0.50
		1:100	0.61	4.33	1.17	0.99	0.94	0.92	3.7	0.93
		1:200	0.62	4.87	1.53	1.35	1.33	1.32	3.7	1.33
Tokomaru	*	1:12½	0.76	0.37	0.24	0.28	0.26	0.30	0.1	0.27
fine sandy loam		1:12½	0.58	0.51	0.33	0.27	0.27	0.30	0.3	0.28
		1:100	0.61	0.87	0.65	0.59	0.57	0.57	0.4	0.57
		1:200	0.56	0.93	0.59	0.61	0.62	0.61	0.3	0.61
Omakere	*	1:12½	0.58	0.56	0.43	0.46	0.50	0.44	0.1	0.44
clay loam		1:12½	0.67	1.16	0.52	0.46	0.45	0.45	0.8	0.45
		1:100	0.68	2.12	1.10	0.91	0.91	0.89	1.4	0.90
		1:200	0.69	2.34	1.17	1.15	1.17	1.16	1.2	1.16
Idaburn		1:12½	0.61	1.90	1.10	0.58	0.51	0.49	2.0	0.50
fine sandy loam		1:100	0.65	2.78	1.10	0.93	0.94	0.93	2.0	0.93
		1:200	0.67	3.01	1.15	1.05	1.06	1.05	2.0	1.05
Timaru		1:12½	0.31	0.94	0.46	0.39	0.40	0.42	0.6	0.40
silt loam		1:100	0.30	1.55	0.90	0.93	0.88	0.88	0.7	0.88
		1:200	0.29	1.75	0.98	0.90	0.92	0.92	0.8	0.92
Halcombe		1:12½	0.53	1.02	0.64	0.41	0.38	0.37	0.9	0.38
silt loam		1:100	0.52	1.82	0.94	0.82	0.78	0.76	1.2	0.77
		1:200	0.54	1.94	0.89	0.84	0.82	0.84	1.1	0.84
Matamau		1:12½	0.51	0.26	0.20	0.18	0.18	0.18	0.1	0.18
silt loam		1:100	0.55	0.59	0.41	0.42	0.42	0.41	0.2	0.41
		1:200	0.52	0.73	0.44	0.44	0.44	0.44	0.3	0.44
Waipara		1:12½	0.62	1.89	0.89	0.63	0.56	0.55	1.8	0.55
silt loam		1:100	0.65	2.87	1.28	1.16	1.08	1.06	2.1	1.07
		1:200	0.61	3.07	1.09	1.11	1.06	1.08	2.0	1.07
Himatangi		1:12½	0.30	0.64	0.33	0.31	0.33	0.31	0.3	0.32
coarse sand		1:100	0.30	1.01	0.80	0.69	0.69	0.68	0.4	0.69
		1:200	0.33	1.20	0.97	0.97	0.88	0.93	0.3	0.93

* Exchangeable potassium removed with N ammonium acetate, pH 7.0.

At the soil to acid ratio of 1:100, much greater amounts of potassium were extracted in all extractions compared with the 1:12½ ratio. The overall pattern of extraction was similar to that at a ratio of 1:12½, except that the difference between the first and successive extracts was more marked and the difference, if any, between the second and successive extracts was less marked. In many cases, constant rates of extraction prevailed after the first extraction.

The extractions at a soil to acid ratio of 1:200 were closely similar to those at 1:100, except that the rates of extraction were slightly higher for the Middlehurst silt loam, Omakere clay loam and Himatangi coarse sand, indicating that with the above exceptions, the maximum rate of reaction had been reached with the 1:100 ratio of soil to acid.

DISCUSSION OF FORM OF EXTRACTION GRAPHS

Two possible explanations of the extraction data are as follows. The first, that the initial N HNO_3 extraction removes potassium and in so doing creates a strongly potassium fixing substance which in subsequent extractions fixes enough of the potassium liberated by the acid to produce an equilibrium mixture with an almost constant concentration of potassium. The second is that there are two forms of nonexchangeable potassium extracted by N HNO_3, a slightly soluble form extracted at a constant rate and a more soluble form extracted almost entirely in the first extractions.

Assuming that the first explanation is correct, and that a definite proportion of the potassium liberated or in solution is refixed, it may be shown that the following relationships exist.

?

If a = K liberated in the first digestion, and
b/a = proportion of K refixed,
Then the amount of K in solution at the end of any extraction is

$$K_n = (a-b)^n / a^{n-1} \quad .$$

If the amount of refixation is small, $a \gg b$, and $K_n \doteq a - nb$.
If the amount of refixation is such that $a = 2b$, $K_n = b / 2^{n-1}$.
If the amount of refixation is large so $a \doteq b$, and $a - b = x$,
then $K_n = x^n / a^{n-1} \longrightarrow 0$ when $x \rangle 2$.

The type of extraction sequence dictated by these 3 equations may be shown if it is assumed that

$a = 1.00$ and that $b = 0.10$, 0.50 and 0.90.

For the above values of a and of b, the successive extractions would contain

b = 0.10	K_n = 0.90,	0.80 ,	0.70 ,	0.60 ,	0.50
b = 0.50	K_n = 0.50 ,	0.25 ,	0.12 ,	0.06 ,	0.03
b = 0.90	K_n = 0.10 ,	0.01 ,	0.00 ,	0.00 ,	0.00,

Calculated on the basis of the first extraction being 1.00 these would become

$b = 0.10$ $K_n = 1.00$, 0.89 , 0.78 , 0.67 , 0.56
$b = 0.50$ $K_n = 1.00$, 0.50 , 0.25 , 0.12 , 0.06
$b = 0.90$ $K_n = 1.00$, 0.10 , 0.01 , 0.00 , 0.00 .

Unless the potassium fixing substance suffered considerable destruction during digestion, none of the above would fit the recorded data. Further, the addition of potassium to the extracting solution should result in considerable fixation with consequent low recovery figures, a fact which was observed (see Table 33), and the subsequent extract should contain more potassium than a similar one not preceded by a potassium addition. In fact, no difference was observed in this case. It is probable, therefore, that the first hypothesis is not valid.

"STEP" POTASSIUM AND "CONSTANT RATE" POTASSIUM

The second explanation, viz. that 2 forms of potassium of very different solubility are extracted, is more in accord with the experimental data. When the amount of potassium per extraction is plotted against the extraction number, the appearance of the graph is that of a constant level preceded by one or more steps above it (Figure 17).

If it is assumed that the constant level is equal to the rate of extraction of the less soluble form of potassium, then the more soluble portion will be represented by the sum of potassium extracted in excess of this value. For convenience, the potassium extracted at a constant rate is called "constant rate" potassium and the potassium extracted in excess of this rate in the first extracts is called the "step" potassium.

A comparison of the extraction data at the soil to acid ratios of 1:12½, 1:100 and 1:200, shows that the "step" potassium is nearly the same for each ratio, and that the "constant rate" potassium increases with the widening ratios.

In the leaching experiments, a nearly constant rate of extraction was recorded after 30 - 60 minutes leaching (Figure 15). If this rate corresponds to the "constant rate" potassium under leaching, then extrapolation back to zero volume of this constant rate of extraction should give the equivalent of the "step" potassium of batch extractions. Inspection of the cummulative volume curves shows that the leaching "step" potassium is nearly identical with the batch "step" potassium.

The dependence of the potassium leached on the volume of leachate at slow to medium leaching rates, shows that the "step" potassium is not of unlimited solubility. With batch extractions, this is shown also. At the narrower soil to acid ratios, more extractions are necessary to remove the "step" potassium, e.g. at a soil to acid ratio of 1:12½, up to 4 extractions may be necessary to extract all the "step" potassium, whereas

FIGURE 17.

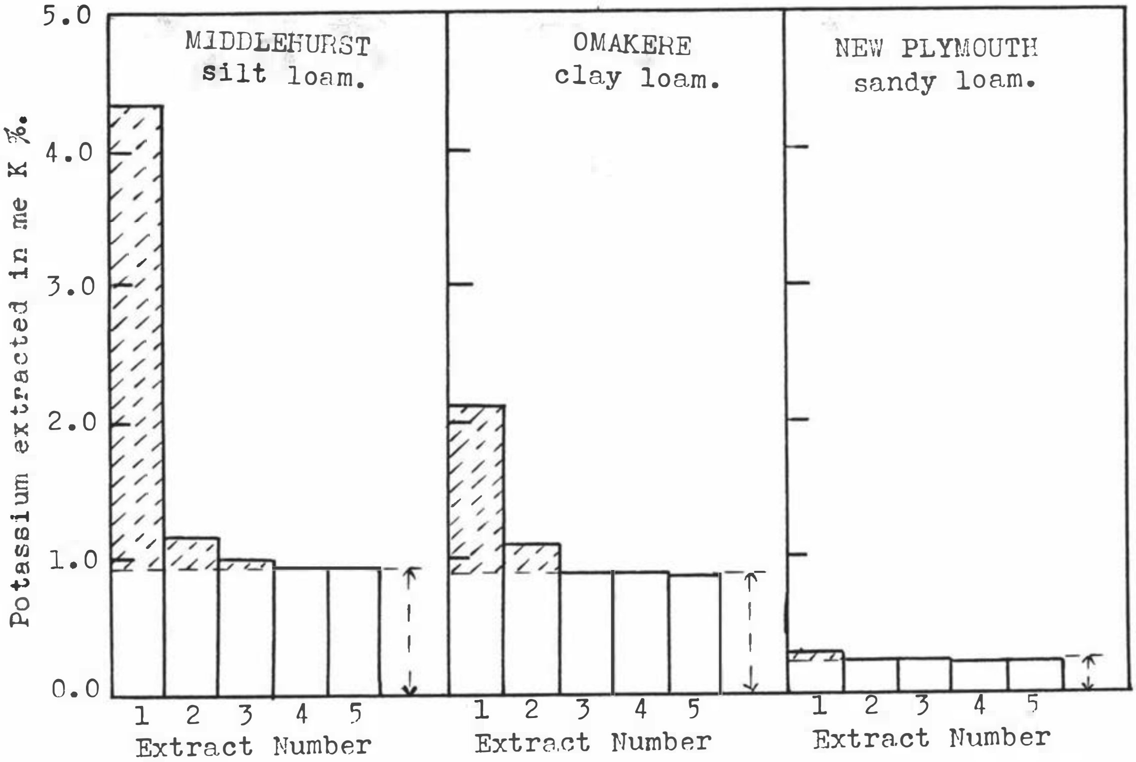


Fig.17.- Potassium soluble in N HNO_3; ratio of soil to acid 1:100, Exchangeable potassium removed with N / 10 HNO_3 prior to first digestion.

A - B.........."Constant Rate" Potassium.
Hatched area..."Step" Potassium.

at a ratio of 1:100, the "step" potassium is removed almost entirely in 2 extractions.

Whereas the "constant rate" potassium is seen to be a function of the soil to acid ratio or the leaching rate and is characteristic of each soil only when the ratio of soil to acid is very wide (1:100 or greater), the "step" potassium is a definite fraction, independent of the time of heating, acid concentration, ratio of soil to acid and of the method of extraction.

POTASSIUM SOLUBLE IN NITRIC ACID FROM CLAYS, SILTS AND SANDS

Rouse and Bertramson (1949) and Pratt (1952) showed that potassium was extracted from all texture fractions on digestion with N HNO_3, with the amount of potassium extracted increasing with increasing fineness of texture. Although variations in the texture of the soils, prevented any exact general partition of the total potassium extracted from the whole soils to the different texture fractions, about one half of the potassium extracted was attributed to the clay fractions. In the present study, extraction of the texture fractions, coarse sand, fine sand, silt and clay, separated from the soils used for the long term cropping experiment, at a range of solid to acid ratios, confirmed that potassium was extracted from all fractions with the greatest amounts per unit weight being extracted from the clay fractions (Tables 19, 20, 21 and 22).

The coarse sands gave "constant rate" potassium values close to those found for the corresponding fine sands. Except for the sands from the Middlehurst silt loam, the "step" potassium for the coarse sands was much less than that for the fine sands. Two coarse sands showed no "step" potassium.

The coarse sand from the Middlehurst silt loam on inspection under microscope, was seen to be largely aggregates of fine sand size crystals joined by a matrix of indefinite composition but apparently of sesquioxides, closely resembling limonite. On digestion with $\underline{N}$ HNO_3, this matrix dissolved producing a solution very high in iron and leaving a residue, predominately fine sand. The large amount of potassium liberated in the first and second extractions is presumed to have come from this macrostructure breakdown, which by observation was complete after 2 extractions. The other coarse sands extracted, i.e. Taupo, Omakere, Idaburn and Himatangi, were predominately of single grain structure of composition similar to the fine sand, but with the Idaburn coarse sand, no noticeable amounts of micas were present.

The extraction patterns of the fine sands (Table 20), showed only a superficial resemblence to those of the whole soils. The "constant rate" potassium was less than that for the whole soils at comparable ratios and the "step" potassium, where present, was less than that for the whole soils, except for the Himatangi coarse sand, which is mainly sand (ca. 95%). Where the fine sands were extracted at more than one sand to acid ratio, it was noticeable that increasing the ratio of acid to sand, produced little change in the amount of potassium extracted at ratios wider than 1:12½ for the Taupo and Tokomaru fine sands, and 1:25 for the Omakere fine sand, but that digestion at the ratio 1:100 extracted more "constant rate" potassium from the Middlehurst and Idaburn fine sands than did digestion at a ratio of 1:50.

Inspection of Table 21, which sets out the extraction data for the silt fractions, shows that all the silts extracted, had appreciable "step" potassium, with the exceptions of the Tokomaru and Timaru silts which had "step" potassium values of 0.0 me K% and 0.2 me K% respectively. The "constant rate" potassium was one and a half to three times that of the corresponding fine sands, except for the Waipara silt loam, where both the silt and fine sand had approximately the same "constant rate" potassium. With the five soils where the silts were extracted at more than one silt to acid ratio, increasing the amount of acid increased the "constant rate" potassium. With the two silts which liberated large amounts of potassium to the first $\underline{N}$ HNO_3 extractions, viz. the Middlehurst and Idaburn silts, the "step" potassium is only an approximation at the narrower ratios as no constant level of extraction had been reached in five extractions.

TABLE 19

POTASSIUM SOLUBLE IN NORMAL NITRIC ACID FROM COARSE SANDS

Time of Heating 15 minutes.

Coarse sand separated from	Ratio	Extract Number 1	2	3	4	5	"Step" K.	"Constant rate" K.
		me%	me%	me%	me%	me%		
Taupo sand	1:12½	0.08	0.08	0.07	0.09		0.0	0.08
Middlehurst silt loam	1:12½	1.59	0.73	0.21	0.19	0.18	1.9	0.19
Omakere clay loam	1:12½	0.20	0.20	0.20	0.19	0.18	0.0	0.18
Idaburn fine sandy loam	1:12½	0.26	0.14	0.14	0.16	0.16	0.1	0.15
Himatangi coarse sand	1:100	0.65	0.40	0.40	0.41		0.2	0.40

TABLE 20

POTASSIUM SOLUBLE IN NORMAL NITRIC ACID FROM FINE SANDS

Time of Heating 15 minutes.

Fine sand separated from	Ratio	Extract Number 1	2	3	4	5	"Step" K.	"Constant rate" K.
		me%	me%	me%	me%	me%		
New Plymouth sandy loam	1:12½	0.15	0.12	0.13	0.12		0.0	0.12
Taupo sand	1:12½	0.14	0.08	0.05	0.05		0.1	0.05
	1:100	0.18	0.12	0.10	0.10		0.1	0.10
Middlehurst silt loam	1:5	0.98	0.90	0.71	0.41	0.26	-	-
	1:12½	1.49	0.82	0.47	0.41	0.32	-	-
	1:25	2.08	1.20	0.75	0.60	0.58	2.2	0.59
	1:50	2.45	1.27	1.05	0.72	0.75	2.3	0.74
	1:100	3.01	0.98	0.97	0.95	0.95	2.2	0.95
Tokomaru fine sandy loam	1:5	0.11	0.11	0.09			0.0	0.10
	1:12½	0.22	0.17	0.19	0.18	0.17	0.0	0.18
	1:25	0.25	0.19	0.21	0.18	0.20	0.0	0.20
	1:50	0.24	0.18	0.18	0.19	0.19	0.0	0.19
	1:100	0.25	0.19	0.18	0.18		0.1	0.18
Omakere clay loam	1:5	0.40	0.18	0.13	0.13		0.3	0.13
	1:12½	0.48	0.24	0.24	0.24	0.20	0.3	0.24
	1:25	0.56	0.33	0.30	0.31	0.30	0.3	0.30
	1:50	0.60	0.35	0.30	0.30	0.30	0.3	0.30
	1:100	0.60	0.45	0.39	0.38		0.3	0.37
Idaburn fine sandy loam	1:5	0.72	0.45	0.25	0.15	0.14	1.0	0.14
	1:12½	0.84	0.54	0.44	0.26	0.26	1.0	0.26
	1:25	1.08	0.52	0.38	0.42	0.35	1.0	0.38
	1:50	1.26	0.81	0.50	0.48	0.48	1.1	0.48
	1:100	1.42	0.68	0.65	0.62		0.8	0.65
Timaru silt loam	1.100	0.45	0.27	0.31	0.28		0.2	0.28
Halcombe silt loam	1:100	0.60	0.41	0.31	0.27		0.4	0.29
Matamau silt loam	1:100	0.19	0.18	0.14	0.15		0.0	0.15
Waipara silt loam	1:100	1.12	0.95	0.82	0.80		0.5	0.80
Himatangi coarse sand	1:100	1.09	0.59	0.61	0.59		0.5	0.59

TABLE 21

POTASSIUM SOLUBLE IN NORMAL NITRIC ACID FROM SILTS

Time of Heating 15 minutes.

Silt separated from	Ratio	Extract Number					"Step" K.	"Constant rate" K.
		1	2	3	4	5		
		me%	me%	me%	me%	me%	me%	me%
Taupo sand	1:12½	0.53	0.20	0.18	0.19		0.3	0.19
	1:100	0.51	0.28	0.22	0.21		0.4	0.22
	1:160	0.54	0.29	0.23	0.22		0.4	0.23
Middlehurst silt loam	1:12½	2.40	1.71	1.01	0.65	0.53	3.6	0.53
	1:100	4.80	1.57	1.34	1.31		3.7	1.32
	1:160	4.70	1.90	1.70	1.53	1.51	3.8	1.52
Tokomaru fine sandy loam	1:12½	0.25	0.27	0.27	0.21	0.28	0.0	0.27
	1:100	0.36	0.32	0.29	0.34	0.35	0.0	0.34
	1:160	0.39	0.37	0.45	0.45		0.0	0.45
Omakere clay loam	1:12½	0.36	0.50	0.41	0.33	0.35	0.7	0.34
	1:100	1.43	1.20	1.01	0.87	0.89	0.7	0.88
	1:160	1.78	1.23	1.15	1.12		0.7	1.13
Idaburn fine sandy loam	1:12½	2.86	2.20	1.69	1.05	0.93		
	1:50	4.12	2.55	2.06	1.66	1.55	4.3	1.55
	1:100	5.65	2.40	1.66	1.66		4.7	1.66
	1:160	5.55	2.62	1.70	1.67		4.7	1.68
Timaru silt loam	1:100	0.57	0.46	0.47	0.46		0.1	0.46
Halcombe silt loam	1:100	0.82	0.52	0.47	0.44		0.5	0.45
Matamau silt loam	1:100	0.43	0.23	0.28	0.26		0.2	0.26
Waipara silt loam	1:100	1.68	1.08	0.89	0.84		1.0	0.86
Himatangi coarse sand	1:100	1.84	0.94	0.89	0.89		1.0	0.89

The "step" potassium for the four silts other than the Idaburn was virtually independent of the silt to acid ratio.

With the exception of the clay isolated from the Taupo sand, which was extracted at a clay to acid ratio of 1:12½ only, all the clays extracted liberated large amounts of potassium (Table 22), far more than did the corresponding silts. The difference was most noticeable in the "step" potassium and to a lesser extent in the "constant rate" potassium. At the ratios 1:12½ and 1:100, no constant rate of extraction was evident,

TABLE 22

POTASSIUM SOLUBLE IN NORMAL NITRIC ACID FROM CLAYS

Time of Heating 15 minutes.

Clay separated from	Ratio	Extract Number 1	2	3	4	5	"Step" K.	"Constant rate" K.
		me%	me%	me%	me%	me%	me%	me%
Taupo sand	1:12½	0.74	0.54	0.43	0.30		0.7	0.30
Middlehurst silt loam	1:12½	4.43	4.09	2.36	1.18	0.73		
	1:100	8.5	2.52	1.54	1.20	0.92		
	1:200	11.7	2.98	1.99	1.78	1.74	11.3	1.76
Tokomaru fine sandy loam	1:12½	0.86	0.78	0.44	0.41	0.34		
	1:100	1.83	1.34	1.35	1.15	1.00		
	1:200	4.02	2.52	2.23	2.14	2.15	2.4	2.14
Omakere clay loam	1:12½	0.76	0.54	0.45	0.65	0.57		
	1:12½	0.67	0.59	0.36	0.47	0.44		
	1:100	2.70	1.65	1.48	1.30	1.17	2.3	1.2
	1:200	5.23	3.26	3.01	2.72	2.67	3.5	2.7
Idaburn fine sandy loam*	1:12½	5.71	3.88	2.35	2.00	1.15		
	1:100	8.8	5.28	3.74	2.90	2.82	9.5	2.85
	1:100	11.8	6.05	3.70	2.75	2.70	12.4	2.72
	1:200	13.5	4.72	3.58	2.87	2.91	13.1	2.90
Timaru silt loam	1:200	6.32	3.86	3.50	3.32	3.20	4.2	3.20
Halcombe silt loam	1:200	6.38	3.89	3.36	2.92	2.85	4.8	2.90
Matamau silt loam	1:200	3.65	2.22	1.52	1.48	1.49	2.9	1.49
Waipara silt loam	1:200	11.1	5.48	4.05	3.48	3.35	10.3	3.4
Himatangi coarse sand	1:200	4.50	2.70	1.75	1.75		3.7	1.75

* Ammonium clay

the fourth extract containing considerably more potassium than the fifth for the Middlehurst and Tokomaru clays and to a lesser extent, for the Idaburn clay. The Omakere clay at the ratio 1:12½, gave erratic results with considerable differences between duplicate extractions (see Table 22). Also at the clay to acid of 1:100, no constant rate was found in 5 extractions. At the clay to acid ratio of 1:200, a constant rate of extraction occurred from the third extraction with the Tokomaru, Matamau and Himatangi clays and for the fourth and fifth extractions, with a tendency for a small drop (0.05-0.10 me K %) to the fifth, for the Middlehurst, Omakere, Idaburn, Timaru, Halcombe and Waipara clays. The "constant rate"

TABLE 23

SUMMARY OF THE "STEP" POTASSIUM AND "CONSTANT RATE" POTASSIUM FOR SOILS AND THEIR TEXTURE SEPARATES

Soil		Coarse Sand	Fine Sand	Silt	Clay	Whole Soil Calc.	Whole Soil Actual	
		me%	me%	me%	me%	me%	me%	
Ratio 1:12½								
Taupo	Step	0.00	0.10	0.35	0.7	0.14	0.14	
sand	C.r.	0.08	0.06	0.19	0.3(a)	0.09	0.09	
Middlehurst	Step	1.9	1.9	3.3	N.A.	-	3.8	
silt loam	C.r.	0.19	0.32	0.64	0.7	0.43	0.50	
Tokomaru	Step	-	0.0	0.0	N.A.	-	0.3	
	C.R.	-	0.18	0.27	0.4	0.22	0.28	
Omakere	Step	0.0	0.24	0.7	N.A.	-	0.8	
clay loam	C.R.	0.18	0.24	0.34	0.5	0.30	0.45	
Idaburn	Step	0.10	1.0	4.2	N.A.	-	2.0	
fine sandy loam	C.R.	0.15	0.26	0.95	1.2	0.40	0.50	
Ratio		1:12½	1:100	1:100	1:200		1:100	1:200
Taupo	Step	0.00	0.10	0.35	0.7 (a c)	0.14	0.18	0.19
sand	C.R.	0.08	0.10	0.22	0.3	0.12	0.15	0.22
Middlehurst	Step	1.9	2.1	3.7	11.3	4.05	3.7	3.7
silt loam	C.R.	0.19	0.95	1.32	1.75	1.02	0.93	1.33
Tokomaru	Step	-	0.05	0.0	2.3	0.4	0.4	0.3
fine sandy loam	C.R.	-	0.19	0.56	2.15	0.59	0.57	0.61
Omakere	Step	0.0	0.30	0.7	3.3	1.4	1.4	1.2
clay loam	C.R.	0.18	0.33	0.89	2.70	1.15	0.90	1.16
Idaburn	Step	0.10	0.88	4.7	13.1	2.19	2.0	2.0
fine sandy loam	C.R.	0.15	0.62	1.65	2.90	0.84	0.93	1.05
Timaru	Step	-	0.17	0.1	3.8	0.80	0.7	0.8
silt loam	C.R.	-	0.28	0.46	3.26	0.86	0.88	0.92
Halcombe	Step	-	0.4	0.4	4.9	1.11	1.3 ?	1.1
silt loam	C.R.	-	0.29	0.45	2.90	0.75	0.77	0.84
Matamau	Step	-	0.0	0.15	2.5	0.42	0.2	0.3
silt loam	C.R.	-	0.15	0.26	1.54	0.34	0.41	0.44
Waipara	Step	-	0.2	1.0	10.4	1.95	2.15	2.0
silt loam	C.R.	-	0.90	0.85	3.40	1.10	1.07	1.07
Himatangi	Step	0.25(b)	0.5	1.0	3.7	0.37	0.4	0.3
	C.R.	0.40(b)	0.60	0.89	1.75	0.50	0.69	0.92

(a) Approximation only as rate of extraction not constant.

(b) Ratio 1:100

(c) Ratio 1:12½

potassium was large for all clays, 1.4-3.5 me K %. The "step" potassium, which because constancy was reached only in the fourth and fifth extracts, must be an approximation, is in all cases very much larger than for the silt. Because from the data available, it is not possible to decide the "constant rate" potassium at ratios less than 1:200 for the Middlehurst, Tokomaru and Omakere clays, a comparison cannot be made between the "step" potassium at the different ratios.

INTEGRATION OF POTASSIUM SOLUBILITY DATA FOR TEXTURE SEPARATES

In Table 23, the "step" potassium and "constant rate" potassium for the whole soil and for the four texture separates and the "step" potassium and the "constant rate" potassium for the whole soil, calculated from the weighted values of the "step" potassium and the "constant rate" potassium of the texture separates for the two solid to acid ratios of 1:12½ and 1:100 are presented. The weighted contributions of the different texture separates to the total potassium extracted are given in Table 24.

TABLE 24

WEIGHTED CONTRIBUTIONS OF THE TEXTURE SEPARATES TO THE "STEP" POTASSIUM AND TO THE "CONSTANT RATE" POTASSIUM OF WHOLE SOILS

Soil	Ratio	Coarse sand 1:12½	Fine sand 1:100	Silt 1:100	Clay 1:200	Sum of Fractions	Percentage from clay
		me%	me%	me%	me%	me%	me%
Taupo sand	Step	0.00	0.06	0.04	0.04(c)	0.14	24
	C.R.	0.02	0.06	0.03	0.01(c)	0.12	8
Middlehurst silt loam	Step	0.30	0.63	0.92	2.2	4.05	55
	C.R.	0.03	0.32	0.32	0.35	1.02	35
Tokomaru fine sandy loam	Step	-	0.02	0.00	0.4	0.4	95
	C.R.	-	0.08	0.09	0.42	0.59	71
Omakere clay loam	Step	0.00	0.07	0.25	1.06	1.38	77
	C.R.	0.01	0.08	0.27	0.79	1.15	69
Idaburn fine sandy loam	Step	0.01	0.53	0.68	0.97	2.19	44
	C.R.	0.02	0.36	0.24	0.22	0.84	26
Timaru silt loam	Step	-	0.07	0.03	0.70	0.80	87
	C.R.	-	0.12	0.14	0.60	0.86	70
Halcombe silt loam	Step	-	0.16	0.10	0.85	1.11	77
	C.R.	-	0.12	0.11	0.52	0.75	69
Matamau silt loam	Step	-	0.0	0.04	0.38	0.42	90
	C.R.	-	0.05	0.06	0.23	0.34	68
Waipara silt loam	Step	-	0.08	0.22	1.65	1.95	85
	C.R.	-	0.38	0.18	0.54	1.10	49
Himatangi coarse sand	Step	0.11(b)	0.20	0.02	0.04	0.37	11
	C.R.	0.18(b)	0.26	0.02	0.04	0.50	8

(b) Ratio 1:100

(c) Ratio 1:12½

Although on a unit weight basis, the clay fraction showed a much greater reactivity than the other fractions, on a weighted basis, the contributions of the clay fractions to the total "step" potassium and to the "constant rate" potassium fell into 3 groups as follows.

TABLE 25

SUMMARY OF PROPORTIONS OF "STEP" POTASSIUM AND OF "CONSTANT RATE" POTASSIUM DERIVED FROM CLAYS

"Step" K	Less than 1/4	Approx. 1/2	More than 3/4
"Constant rate" K	Less than 1/10	1/4 - 1/3	1/2 - 3/4
	Taupo sand Himatangi coarse sand	Middlehurst silt loam Idaburn fine sandy loam	Tokomaru fine sandy loam Omakere clay loam Timaru silt loam Holocombe silt loam Matamau silt loam Waipara silt loam Middlehurst silt loam (deferrated)

The group where the clay makes a negligible contribution to the potassium extracted, contains 2 coarse textured soils with very low clay percentages, viz 2.9% and 2.4%.

The second group contains 2 soils, the Idaburn fine sandy loam, of which 61% is fine sand containing appreciable amounts of mica, and the Middlehurst silt loam, the coarse and fine sands of which, when prepared by the standard dispersion methods contain appreciable numbers of aggregates of clay and mineral grains.

The third group contains the bulk of the samples analysed, indicating that in most loam soils, the clay fraction is the most important source of acid soluble potassium.

The above comparisons are based on extractions at ratios of 1:100 for the fine sands and silts and 1:200 for the clays. Because the "step" potassium is virtually independent of the ratio at 1:100 and 1:200, there will be little bias in favour of the clays. The contribution of the clays to the "constant rate" potassium figures will be over-emphasised to some extent.

During the extraction of the coarse and fine sands from the Middlehurst silt loam, it was apparent that large amounts of silt and clay size particles were formed in the first and second digestions. Microscopic examination of the coarse and fine sands showed that, as stated earlier, the coarse sand was largely aggregates of single grain crystals joined by a limonite-like matrix and that the fine sand particles were covered with a clay like coating and that there were fine sand size aggregates similar to those seen in the coarse sand.

It was apparent that more efficient deferration and dispersion would have given a mechanical analysis lower in sand and richer in clay and silt. A 10 gm. sample of Middlehurst silt loam was dispersed, after destruction of organic matter, by agitating for 10 minutes in a milkshake machine with calgon and sodium carbonate added. The clay was separated by decantation and the sands and silt deferrated by Matelski's method (see page 30) and the resulting deferrated coarse and fine sands, silt and clay separated by sedimentation. The clay was added to that separated originally. Table 26 shows the change in mechanical analysis brought about by deferration.

TABLE 26

MECHANICAL ANALYSIS OF THE MIDDLEHURST SILT LOAM. BEFORE AND AFTER DEFERRATION

	Coarse sand	Fine sand	Silt	Clay
Not deferrated.	15.9	32.8	22.2	20.6
Deferrated.	8.4	28.2	28.6	24.0

Note: Percentages based on oven dry soil containing 7.7% O.M.

The texture separates from the above dispersion were extracted with $\underline{N}$ HNO_3 at ratios of 1:12½ for the coarse sand, 1:100 for the fine sand and silt and 1:200 for the clay (Table 27).

TABLE 27

POTASSIUM SOLUBLE IN NORMAL NITRIC ACID FROM TEXTURE SEPARATES FROM MIDDLEHURST SILT LOAM

Fraction		Extract Number 1	2	3	4	5	"Step" K.	"Constant rate" K.
		me%	me%	me%	me%	me%	me%	me%
Coarse sand	Def.	0.43	0.19	0.16	0.17	0.18	0.26	0.17
	Not Def.	1.59	0.73	0.21	0.19	0.18	1.9	0.19
Fine sand	Def.	2.00	0.97	0.88	0.90	0.91	1.15	0.90
	Not Def.	3.01	0.98	0.97	0.95	0.95	2.1	0.95
Silt	Def.	4.50	1.50	1.29	1.25	1.30	3.45	1.28
	Not Def.	4.80	1.57	1.34	1.31	1.32	3.7	1.32
Clay	Def.	11.5	3.12	2.04	1.81	1.77	11.3	1.8
	Not Def.	11.7	2.98	1.99	1.78	1.74	11.3	1.75

One difference between the deferrated and undeferrated fractions was noticeable during the extractions. The considerable amounts of finer fractions which were formed during the extraction of undeferrated coarse and fine sands, were virtually absent during the above extractions. While the "constant rate" potassium was the same within experimental error for the deferrated and undeferrated texture separates, the "step" potassium of the sand fractions was reduced greatly, that of the coarse sand from 1.9 me K % to 0.26 me K % and that of the fine sand from 2.1 me K % to 1.15 me K %. On the basis of potassium extracted from deferrated separates, the proportion of the "step" potassium and of the "constant rate" potassium of the whole soil which came from the clay, rose from 58% to 66% of the "step" potassium and from 35% to 40% of the "constant rate" potassium.

The effect of deferration on the fine sand fractions of a further six soils is shown in Table 23.

TABLE 23

THE EFFECT OF DEFERRATION OF FINE SANDS ON THE POTASSIUM SOLUBLE IN NORMAL NITRIC ACID

Ratio of fine sand to acid 1 : 100.

Fine sand separated from		Extract number 1	2	3	4	Yield of deferrated fine sand.
		me%	me%	me%	me%	
Tokomaru fine sandy loam	Def.	0.24	0.20	0.18	0.18	95%
	Not def.	0.25	0.19	0.18	0.18	
Omakere clay loam	Def.	0.58	0.43	0.41	0.39	94%
	Not def.	0.60	0.45	0.39	0.36	
Idaburn fine sandy loam	Def.	1.33	0.63	0.61	0.60	98%
	Not def.	1.42	0.68	0.65	0.62	
Halcombe silt loam	Def.	0.62	0.44	0.33	0.32	91%
	Not def.	0.60	0.41	0.31	0.27	
Waipara silt loam	Def.	1.14	0.91	0.88	0.86	96%
	Not def.	1.12	0.95	0.82	0.80	
Himatangi coarse sand	Def.	1.04	0.62	0.60	0.63	97%
	Not def.	1.09	0.59	0.61	0.59	

The yield of deferrated fine sand in all cases was of the order of 90% and the differences brought about by deferration were within experimental error. Because the above fine sands were largely single grained crystals with little coating, differences of the order found for the Middlehurst silt loam texture separates were not expected.

POTASSIUM SOLUBLE IN NORMAL NITRIC ACID FROM SOIL MINERALS

Although the potassium extracted by N HNO_3 has been partitioned between the texture separates, the contribution of the various soil minerals to the potassium extraction values is also required if the source of the acid soluble potassium is to be determined.

Accordingly, samples of the clay minerals, illite, kaolinite and montmorillonite, and the potassium-rich minerals, vermiculite, biotite, muscovite and orthoclase, were ground to sizes comparable with those found in "fine earth" (< 2mm.) and separated into appropriate texture separates.

Although an important soil forming mineral in many overseas soils (see Phillippe and White, 1952), microcline was not extracted because it is not an important component of New Zealand rocks, occurring only in granites and in small amounts in some greywackes (Reed, personal communication). In the microscopic examination of the fine sand separated from the soils used for cropping, no evidence of microcline was found.

In all cases, prior to extraction with N HNO_3, any exchangeable potassium present was removed by extraction with N/10 HNO_3. The results of extracting the above minerals are given in Table 29.

The clay minerals, kaolinite and montmorillonite, prepared from geological specimens and therefore not necessarily identical with soil-clay minerals of the same names, at the clay to acid ratio of 1:100, showed very small "step" potassium and "constant rate" potassium values, 0.1 me K% and 0.11 me K% for kaolinite and 0.10 me K% and 0.14 me K % for montmorillonite. If the assumption that these geological speciments of the clay minerals are essentially similar to the soil-clay minerals is justified, neither clay mineral would contribute much potassium to that extracted from the clay fractions.

On the other hand, illite would appear to be capable of supplying the "step" potassium and "constant rate" potassium for all the soil clays tested other than those from the Middlehurst, Idaburn and Waipara soils.

The micas, vermiculite and biotite, reacted similarly on digestion with N HNO_3, dissolving completely, leaving a very small residue of siliceous scales, in two extractions at the ratio of 1:1000. The potassium extracted from each mineral would therefore appear entirely as "step" potassium.

Muscovite on extraction with N HNO_3 yielded potassium at a constant rate after two extractions. The amount of "step" potassium was dependent on the particle size, varying from 1.9 me K% for the coarse sand to 7.4 me K% for the fine sand and to 15.9 me K% for the silt. The "constant rate" potassium also varied inversely with the particle size, increasing from 0.45 me K % for coarse sand at a 1:125 ratio to 3.2 me K % for the fine sand at ratios of 1:250 to 1:100 and to 4.0 me K % at a ratio of 1:1000 for the silt. In contrast to biotite which dissolved leaving a residue of a few extremely fine siliceous scales, muscovite retained its plate-like structure, although considerable exfoliation appeared to have taken place.

Illite resembled muscovite rather than biotite in its reactions towards N HNO_3. Whereas biotite dissolved nearly completely in 2 extractions, only 25% of the illite dissolved in 5 extractions at a ratio of 1:200 and 35% at a ratio of 1:1000. The extractions were of a form similar to those of muscovite.

TABLE 29

POTASSIUM SOLUBLE IN NORMAL NITRIC ACID FROM TYPICAL MINERALS

	Size	Ratio	Exch. K after grinding	Extract number 1	2	3	4	5	"Step" K.	"Constant rate" K.
			me%	me%	me%	me%	me%	me%	me%	me%
Illite	$<2\mu$	1: 200	3.0	13.8	7.2	5.6	5.3	5.4	10.4	5.4
		1:1000	4.5	18.3	8.1	8.1	7.9	8.0	10.3	8.0
Kaolinite	Silt, clay	1: 100	0.18	0.21	0.10	0.11	0.10		0.1	0.10
Montmorillonite	Clay sol	1: 100	1.32	0.34	0.14	0.14	0.16		0.1	0.14
Vermiculite	Coarse sand	1: 100	8.1	45.6	9.2	1.15	0.51	0.10	57	0
		1:1000	10.7	55.8	4.2	0.0	0.0		60	0
Biotite	Fine sand	1:1000	15.7	160	9.5	0.05	0.0		170	0
	Silt	1:1000	29.2	155	3.2	0.0	0.0		158	0
Muscovite	Coarse sand	1: 125	0.4	2.0	0.8	0.45	0.45	0.50	1.9	0.45
	Fine sand	1: 250	1.7	8.8	4.9	3.3	3.0	3.2	7.3	3.2
	Fine sand	1: 800	1.9	9.3	5.7	3.4	3.3	3.3	8.1	3.3
	Fine sand	1:1000	2.2	9.2	5.2	3.5	3.0	3.5	7.4	3.5
	Silt	1:1000	6.8	17.1	6.8	3.7	4.0	4.1	15.9	4.0
Orthoclase	Fine sand	1: 25	0.17	0.34	0.39	0.39	0.39		0.0	0.39
	Fine sand	1: 100	0.20	0.66	0.69	0.67	0.64	0.68	0.0	0.67
	Silt	1: 100	0.43	3.7	3.0	2.8	3.0	3.1	0.7	3.0

Orthoclase, of fine sand size, gave virtually constant extraction figures for all extractions at each ratio, i.e. the "step" potassium was zero. The "constant rate" potassium increased from 0.39 me K % at the 1:25 ratio to 0.66 me K % at the 1:100 ratio. The silt size separate showed a small amount of "step" potassium, 0.7 me K %, with a constant rate of 3.0 me K %.

Summarized, the contributions of the minerals tested are as follows.

TABLE 30

Mineral	"Step" K	"Constant rate" K
Illite	Medium.	High, dependent on ratio
Kaolinite	Very low.	Very low.
Montmorillonite	Very low.	Very low.
Vermiculite	Very high, all K this form.	Nil.
Biotite	Very high, all K this form.	Nil.
Muscovite	Medium, dependent on particle size.	High, dependent on particle size and on ratio.
Orthoclase	Nil for fine sand, low for silt.	Medium, dependent on particle size and on ratio.

These minerals when present in soils, should contribute to the potassium extracted in a manner similar to that shown in Table 30.

The fine sand fraction, being single grained and of a size suitable for microscopy, provides an opportunity for checking the amount of potassium extracted from the soil minerals.

By inspection under the microscope, the fine sand fractions, although seen to contain a wide range of minerals, were found to be mainly quartz, felspars and, in those sands from North Island soils, volcanic glass. With the equipment available, it was not possible to differentiate positively between quartz and the plagioclases with similar refractive indices and specific gravities.

These minerals may be separated into simpler groups by sedimentation in heavy liquids of definite specific gravity. It was found impossible to effect complete separations into specific gravity groups as traces of minerals with specific gravities outside the range required, persisted in spite of considerable replication of the separations. The determination of the reactions of specific minerals were therefore not possible. Also, minerals, not normally regarded as potassium minerals, contain potassium as an impurity, e.g. plagioclases frequently contain 1% or so of potassium (Clarke, 1924) and if soluble in $\underline{N}$ HNO_3 may liberate potassium in sufficient quantity to obscure the reactions of the mineral under consideration.

Enrichment of the separates with regard to one or more minerals affords some indication of their behaviour towards $\underline{N}$ HNO$_3$. Table 31 gives the results of some unreplicated extractions of specific gravity separates from the Middlehurst, Idaburn and Himatangi fine sand fractions. These indicate that on a unit weight basis, the fraction S.G. 2.7-2.9, liberated the greatest amount of potassium to $\underline{N}$ HNO$_3$. Where muscovite (or sericite) was observed, the "constant rate" potassium as well as the "step" potassium was large.

TABLE 31

POTASSIUM SOLUBLE IN NORMAL NITRIC ACID FROM FINE SAND SEPARATES OF KNOWN SPECIFIC GRAVITY

Fine sand separated from	Specific gravity	Ratio	Extract number					Minerals present
			1	2	3	4	5	
			me%	me%	me%	me%	me%	
Middlehurst silt loam	>2.96	1:100	0.83	0.26	0.26	0.25		Fe ore, Ol, Au
	2.96-2.70	1:100	3.01	1.24	1.30	1.42		Ad,Ce Cl,Fe
	<2.70	1:100	2.49	1.02	1.07	1.13		Or,Ad,Q,Ce
Idaburn fine sandy loam	>2.96	1:12½	0.92	0.80	0.59	0.50	0.50	E, H, Cl, B
	2.96-2.69	1:12½	3.09	1.94	1.49	0.85	0.70	M, K, Cl, E, Q
	2.69-2.64	1:12½	0.29	0.06	0.03	0.02	0.02	Q, Ab
	<2.64	1:12½	0.04	0.03	0.03	0.02	0.02	Ab
	>2.96	1:250	1.9	1.5	1.3	1.3	1.2	As above
	2.96-2.69	1:600	9.2	4.3	5.5	5.6	4.7	As above
	<2.69	1:100	0.46	0.06	0.07	0.06	0.03	Q, Ab
Himatangi coarse sand	>2.70	1:100	1.38	0.63	0.67	0.68		Au,H, Fe,Hy
	<2.70	1:100	0.83	0.51	0.53	0.50		Q, P

Key to Minerals See Table 32.

The potassium extracted from the Idaburn separates came virtually entirely from the fractions of specific gravities, 2.7-2.9 and > 2.9, which contained appreciable amounts of muscovite and a brown chloritic material resembling biotite. The fraction, S.G. 2.64, which was entirely albite and quartz, yielded only traces of potassium. Of the seven fine sands which were extracted after deferration, only two, viz. the Middlehurst and the Idaburn fine sand fractions, contained much mica. Both of these had larger than average "step" potassium values for the fine sand.

The absence of micas from the majority of the fine sand fractions shows that for most soils, other sources of potassium are of prime importance. A comparison of the potassium extraction data for the fine sands (Tables 20 and 31) and their mineral content (Tables 3 and 31) shows that the fine sands, rich in acid felspars, mainly orthoclase, viz. those from the Tokomaru fine sandy loam, Omakere clay loam, Timaru silt loam, Halcombe silt loam, Matamau silt loam and Waipara silt loam, have low "step" potassium and with the exception of the fine sand from the Waipara silt loam, have low "constant rate" potassium, just as found for ground orthoclase.

TABLE 32

KEY TO MINERAL ABBREVIATIONS

Abbreviation	Mineral
Ab	Albite
Ad	Andesine
Allo.	Allophane
Au	Augite
B	Biotite
BC	Brown chlorite
Ce	Celadonite (altered glauconite)
Cl	Chlorite
E	Epidote
F	Felspars
Fe	Iron ores, haematite, goethite etc.
Gl	Glass
H	Hornblende
Hal	Meta-halloysite
HM	Hydrous micas
Hy	Hypersthene
Il	Illite
M	Muscovite
Mo	Montmorillonite
Ol	Olivine
P	Plagioclase (andesine - anorthite)
Q	Quartz
S	Colloidal silica
V	Clay-vermiculite

The only observable difference between the mineralogical composition of the fine sand from the Waipara silt loam and from the other felspar rich fine sands was that a small amount ($<$ 5%) of a sericitic mineral was present in the Waipara silt loam fine sand fraction. It is possible that the extra potassium may have been extracted from this micaceous mineral, except that higher "step" potassium than 0.5 me K % would then be expected.

Further, considerable amounts of potassium were extracted by $\underline{N}$ HNO_3 from fractions which contained neither felspars nor micas. For example, the fine sand fraction of the Himatangi coarse sand, S.G. $>$ 2.70, containing mainly pyroxenes and amphiboles but no mica nor felspar, has "step" potassium of 0.7 me K% and a "constant rate" potassium value of 0.07 me K%. The lighter fraction of this soil, containing no orthoclase but only quartz and andesine with a trace of volcanic glass, liberates more potassium than the orthoclase rich fine sands and nearly as much "constant rate" potassium as ground orthoclase.

The results of the investigation into the behaviour of the soil minerals when extracted with $\underline{N}$ HNO_3 tend to confirm the conclusions based on the extraction of powdered geological specimens that the micaceous minerals such as illite and by inference, intermediates such as clay vermiculite, are the main source of acid soluble potassium. From the limited information available about the clay mineral distribution in the soils studied, it is not possible to develop any definite quantitative relationship between the clay minerals and the potassium extracted.

THE EFFECT OF CATIONS ON THE AMOUNT OF POTASSIUM EXTRACTED

The amount of potassium extracted by nitric acid from the different soils and texture fractions has been shown to be dependent on the conditions of extraction, with the greatest amount of potassium extracted in the first extraction. A notable inconsistency with the general pattern of extractions was found where neutral normal ammonium acetate was used to remove the exchangeable potassium prior to the first extraction (Table 18). Then the first extracts contained very much less potassium than did those where dilute nitric acid was used to remove the exchangeable potassium for the Middlehurst, Tokomaru and Omahere soils, but approximately the same for the New Plymouth, Taupo and Kiripaka soils.

A similar repression in potassium extracted, was observed with the leaching of soil samples with hot $\underline{N}$ HNO_3 after the exchangeable potassium was removed with ammonium acetate compared with dilute nitric acid.

Two possible causes of the lower potassium values are ✓

1. Lower recovery of potassium where ammonium ions were present in the extracting liquid.
2. Ammonium ions may interfere with the extraction of potassium.

The first possibility was checked by adding known amount of potassium as KCl together with ammonium chloride to the acid extract immediately before centrifuging. Complete recovery of this added potassium proved that ammonium ions did not affect the amount of potassium extracted at or after this stage of the extraction and that any effects must have been caused before this stage. The recovery of potassium added to the dilute nitric acid in the determination of exchangeable potassium was also complete.

Potassium added prior to extraction by N HNO_3 affected considerably the amount of potassium extracted by the acid. Table 33 shows the results of extractions carried out on New Plymouth, Omakere and Timaru soils in the presence of potassium added before each extraction at a soil to acid ratio of 1:12½ and at 1:100. The extractions at the ratio 1:100 were on H-saturated exchangeable potassium freed soils and at 1:12½ on ammonium saturated and on H-saturated exchangeable potassium freed soils.

TABLE 33

EFFECT OF AMMONIUM IONS AND OF POTASSIUM IONS ON POTASSIUM SOLUBLE IN NORMAL NITRIC ACID

Soil		Ratio	K added per extract	Extract number 1	2	3	4
			me%	me%	me%	me%	me%
New Plymouth	NH_4 sat.	1:12½	0	0.35	0.18	0.17	0.17
			1	1.20	1.18	1.20	1.18
	H sat.	1:12½	0	0.23	0.21	0.20	0.19
			1	1.13	1.19	1.19	1.22
	H sat.	1:100	0	0.31	0.25	0.26	0.25
			1	1.36	1.23	1.21	1.22
Omakere clay loam	NH_4 sat.	1:12½	0	0.53	0.43	0.47	0.50
			1	1.35	1.32	1.25	1.23
	H sat.	1:12½	0	1.18	0.52	0.47	0.44
			1	1.92	1.34	1.24	1.22
	H sat.	1:100	0	2.12	1.10	0.91	0.91
			1	2.68	1.63	1.58	1.54
Timaru silt loam	NH_4 sat.	1:12½	0	0.65	0.45	0.40	0.40
			1	1.52	1.26	1.22	1.20
	H	1:12½	0	0.98	0.43	0.37	0.38
			1	1.77	1.25	1.20	1.22
	H sat.	1:100	0	1.55	0.90	0.92	0.89
			1	2.42	1.66	1.62	1.65

The three soils reacted differently in that the potassium extracted from the New Plymouth sandy loam was virtually unaffected by the presence of ammonium or potassium ions, but for both the Omakere clay loam and the Timaru silt loam, the potassium extracted in the presence of added potassium was considerably less than the sum of the added potassium and the potassium extracted by N HNO_3 alone. The depression in potassium extracted in the first extract from ammonium saturated soils compared with H-saturated soils, was also found when potassium was added to the extracting solutions.

Further samples of Omakere clay loam were extracted at a soil to acid ratio of 1:100 with the addition to one extraction only per series of known amounts of potassium and ammonium ions singly and together. As can be seen from Table 34, additions of potassium or of ammonium depressed the amount of potassium extracted and when added together the effects were cumulative. Potassium ions appeared to be more effective than ammonium ions in depressing the amount of potassium extracted. There appeared to be no effect on subsequent extractions, except with the extraction following that containing an addition of 5 me K% plus 5 me NH_4%, which was 0.19 me% above the average for this extraction.

TABLE 34

EFFECT OF ADDED POTASSIUM OR AMMONIUM IONS ON POTASSIUM SOLUBLE IN NORMAL NITRIC ACID

Soil Omakere clay loam
Soil to acid ratio 1:100

Extract Number 1 Ion added		2 Ion added		3 Ion added	
	me%		me%		me%
0	2.12	0	1.10	0	0.91
5me K %	6.35	0	1.10	0	0.88
5me NH_4%	1.70	0	1.10	0	0.85
5me K% plus 5me NH_4%	5.55	0	1.20	0	0.88
2.5 me K plus 2.5me NH_4%	3.32	0	1.12	0	0.88
100me NH_4%	1.17	0	1.08	0	0.88
0	2.10	5 me NH_4%	0.55	0	0.88

A similar effect if produced when the exchangeable potassium is not removed prior to the first extraction, viz. a lower first extraction with no effect on later extracts, would result in a lower estimate of the "step" potassium.

Samples of the New Plymouth sandy loam, Middlehurst silt loam, Omakere clay loam and Timaru silt loam were extracted at a soil to acid ratio of 1:12½ without prior removal of exchangeable potassium. The differences between the potassium extracted by this method and by prior extraction of exchangeable potassium with dilute nitric acid are shown in Table 35. Assuming that subsequent extractions would not be affected by the non-removal of exchangeable potassium, a marked reduction in "step" potassium would result from not removing the exchangeable potassium for 3 of the 4 soils tested.

TABLE 35

EFFECT OF NON-REMOVAL OF EXCHANGEABLE POTASSIUM ON FIRST NORMAL NITRIC ACID EXTRACTION

Soil to acid ratio 1: 12½

Soil.	Exchangeable K.	Extract 1, ex Table 18.	Sum of exch. K and extract 1.	First extract, exch. K not removed.	Difference.
	me%	me%	me%	me%	me%
New Plymouth sandy loam	1.08	0.25	1.33	1.35	-0.02
Middlehurst silt loam	0.62	2.99	3.62	3.26	0.36
Omakere clay loam	0.67	1.16	1.83	1.52	0.31
Timaru silt loam	0.52	0.98	1.50	1.09	0.21

The effect of the cations, sodium, calcium and barium, on the potassium extracted by nitric acid was shown by extraction at a soil to acid ratio of 1:100 with the above ions added at concentrations of 50 me%. Table 36 presents the results of extractions of the New Plymouth sandy loam, Omakere clay loam and Timaru silt loam. The influence of these cations on the extraction of these soils is seen to be very small compared with that of potassium and ammonium, mainly as a small increase in the "constant rate" potassium in the presence of calcium.

TABLE 36

EFFECT OF SODIUM, CALCIUM AND BARIUM IONS ON POTASSIUM SOLUBLE IN NORMAL NITRIC ACID

Soil to acid ratio 1:100

	Cation added	Amount	Extract Number 1	Extract Number 2	Extract Number 3
		me%	me%	me%	me%
New Plymouth sandy loam		0	0.31	0.25	0.26
	Na	50	0.32	0.24	0.24
	Ca	50	0.33	0.27	0.26
	Ba	50	0.26	0.24	0.24
Omakere clay loam		0	2.12	1.10	0.91
	Na	50	2.06	1.13	0.94
	Ca	50	2.14	1.17	0.98
	Ba	50	2.08	1.05	0.89
Timaru silt loam		0	1.55	0.90	0.92
	Na	50	1.53	0.93	0.90
	Ca	50	1.54	0.97	0.94
	Ba	50	1.49	0.94	0.87

A series of extractions of the fine sand, silt and clay from the Idaburn fine sandy loam, fine sand from the Middlehurst silt loam and from the Tokomaru fine sandy loam and ground samples of orthoclase, muscovite, biotite, vermiculite and of illite, with N HNO_3 containing ammonium, potassium or calcium ions, reported in Table 37, shows that the ammonium ion depressed the amount of potassium extracted from all separates

TABLE 37

EFFECT OF ADDED CATIONS ON POTASSIUM SOLUBLE IN NORMAL NITRIC ACID FROM TEXTURE SEPARATES AND SOME MINERALS

Separate or mineral	Ratio	Ions added		Extract number 1	2	3	4	5
			me%	me%	me%	me%	me%	me%
Idaburn fine sand	1:25		0	1.03	0.52	0.38	0.42	0.35
		NH_4	0.2	0.86	0.30	0.28	0.39	
		"	1	0.83	0.29	0.05	0.03	0.02
		"	10	0.77	0.29	0.07	0.01	0.01
		"	100	0.74	0.28	0.06	0.03	0.37
		Ca	10	1.14	0.64	0.52	0.62	
		K	1.0	0.98	0.24	0.14	0.17	0.15
	1:50		0	1.26	0.31	0.50	0.48	0.48
		NH_4	200	0.78	0.28	0.07	0.47	
Idaburn silt	1:50		0	4.12	2.55	2.06	1.56	1.55
		NH_4	200	2.95	1.85	0.60	0.38	1.48
		Ca	20	4.0	2.67	2.00	1.72	1.49
Idaburn clay	H-sat. 1:100		0	11.8	5.05	3.70	2.75	
	NH_4-sat. 1:100		0	3.8	5.28	3.74	2.90	
		NH_4	400	9.05	3.55	2.10	3.20	
Tokomaru fine sand	1:25		0	0.25	0.19	0.21	0.18	0.20
		NH_4	100	0.14	0.09	0.09	0.11	0.21
		K	1.0	0.17	0.10	0.02	0.03	0.01
Middlehurst fine sand	1:25		0	2.08	1.20	0.75	0.60	0.58
		K	1.0	1.76	0.66	0.44	0.34	0.33
Orthoclase fine sand	1:25		0	0.34	0.39	0.39	0.32	
		NH_4	10	0.32	0.32	0.30	0.38	
		Ca	10	0.50	0.45	0.45	0.40	
Muscovite fine sand	1:1000		0	9.2	5.2	3.5	3.0	3.5
		NH_4	100	6.0	3.4	1.8	2.2	2.1
		"	400	6.1	0.5	0.4	0.5	
		Ca	100	9.0	5.6	4.7	4.3	3.9
Biotite fine sand	1:1000		0	160	9	0	0	
		NH_4	400	135	23	10	0	
Vermiculite coarse sand	1:1000		0	55.8	4.2	0	0	
		NH_4	400	53.5	6.0	0	0	
Illite	1:1000		0	18.3	8.1	8.1	7.9	
		NH_4	20	13.0	5.7	4.4	4.8	

Results underlined from extractions without added cations.

Added potassium subtracted from results of all extractions with 1.00me K% added.

and minerals tested. As for whole soils, the calcium ion produced little effect, mainly as a slightly higher rate of extraction.

Comparison of the "step" potassium and the "constant rate" potassium for the acid extractions in the presence of the cations K, NH_4, Ca, Na and Ba, reveals that the "step" potassium is virtually independent of these cations but the "constant rate" potassium is very sensitive to the presence of K and of NH_4 cations.

Therefore, extraction in the presence of large amounts of ammonium ions should result in a reduced "constant rate" potassium but unchanged "step" potassium. Extraction of New Plymouth sandy loam, Omakere clay loam, Idaburn fine sandy loam and Timaru silt loam at a soil to acid ratio of 1:100 with 100 me NH_4 % added before each extraction gave the expected reduction in "constant rate" potassium, but at the expense of requiring more extractions to reach the constant rate of extraction of potassium (Table 32).

TABLE 33

EFFECT OF ADDING 100 me NH_4 % TO EXTRACTING ACID

Soil to acid ratio 1:100

Soil	NH_4 added	Extract number 1	2	3	4	5	"Step" K.	"Constant rate" K.
	me%	me%	me%	me%	me%	me%	me%	me%
New Plymouth	0	0.31	0.25	0.26	0.25	0.25	0.1	0.25
sandy loam	100	0.29	0.24	0.24	0.24	0.23	0.1	0.24
Omakere	0	2.12	1.10	0.91	0.91	0.89	1.4	0.90
clay loam	100	1.12	0.69	0.44	0.36	0.35	1.2	0.36
Idaburn	0	2.78	1.10	0.93	0.94	0.94	2.0	0.93
fine sandy loam	100	1.44	0.95	0.55	0.40	0.36	1.9	0.38
Timaru	0	1.35	0.90	0.93	0.88	0.88	0.7	0.88
silt loam	100	1.14	0.51	0.42	0.47	0.45	0.7	0.45

The extraction data resemble those of extractions at a soil to acid ratio of 1:12½ and show no advantages in comparing soils would be gained by using this extractant instead of pure N HNO_3.

The results reported in this section and in Table 13, emphasize the errors caused by not removing the exchangeable potassium before extraction or by extracting ammonium saturated soils. This will be a variable effect due to certain minerals presumably not present in the New Plymouth sandy loam, Taupo sand and Kiripaka clay loam, but present in the Middlehurst silt loam and the moderately and weakly weathered zonal soils.

POTASSIUM FIXATION

To test the hypothesis that potassium deficiency may be brought about by excessive potassium fixation in the same sense that phosphorus deficiency may be caused by excessive phosphorus fixation, the potassium fixing powers of the soils used in the long-term cropping experiment, were determined by subjecting them to a single cycle of wetting and drying at 105°C in the presence of added potassium, during which approximately 70% of the total fixation should occur (Volk N.J. 1934). Fixation on storage for 1 week in contact with solutions of potassium was also determined.

The potassium fixation was defined as follows

K fixation = exchangeable K before fixation plus K added

less exchangeable K after fixation.

Table 39 summarises the fixing powers found for the 12 soils and 6 minerals tested. Appreciable fixation on drying was found for 8 of the 12 soils

TABLE 39

POTASSIUM FIXING POWERS OF SOILS AND MINERALS

Soil or mineral	Fixation on moist storage. 1me%	5me%	Fixation on drying 0me%	1me%	2½me%	5me%	Increase in "step" K. (Table 40)	"Step" K.
	me%	me%	me%	me%	me%	me%	me%	me%
New Plymouth sandy loam	0.0	-0.1	0.0	0.0	0.0	0.1	0.05	0.05
Taupo sand	0.0	0.0	0.0	0.1	0.2	0.1	0.1	0.15
Kiripaka clay loam	0.0	0.0	0.0	0.1	0.2	0.3	0.25	0.2
Middlehurst silt loam	0.2	0.3	0.0	0.5	1.1	1.0	1.6	3.7
Tokomaru fine sandy loam	0.3	0.7	0.3	0.4	0.9	0.8	0.8	0.4
Omakere clay loam	0.3	0.5	0.0	0.3	0.3	0.6	0.6	1.4
Idaburn fine sandy loam	0.2	0.4	0.0	0.4	0.4	0.4	0.5	2.0
Timaru silt loam	0.1	0.7	0.0	0.5	1.0	1.0	0.9	0.7
Halcombe silt loam	0.0	0.5	0.2	0.4	0.7	0.8	0.6	1.3
Hatuma silt loam	0.1	0.6	0.1	0.5	0.4	0.6	0.6	0.2
Waipara silt loam	0.0	0.6	0.0	0.3	0.3	0.7	0.7	2.1
Himatangi coarse sand	0.0	0.1	0.0	0.1	0.1	0.1	0.1	0.4
Montmorillonite						0.8	0.8	0.2
Kaolinite						0.0	0.0	0.1
Orthoclase						0.0	0.0	0.0
Muscovite						0.0	0.1	7.4
Biotite						0.0	-	170
Vermiculite						0.5	-	57

but only for montmorillonite and vermiculite of the minerals. The greatest fixing capacities were found with the Middlehurst, Timaru and Halcombe silt loams, which were not the soils on which potassium deficiencies were observed in the glasshouse study. The fixation on moist storage varied in the same fashion as the fixation on drying but with the greatest fixation found in the Tokomaru fine sandy loam and the Matamau silt loam. The soils after being subjected to the single wetting and drying cycle with the addition of 5 me K % as KCl, were extracted with dilute nitric acid to remove the exchangeable potassium and then extracted four times with N HNO_3 at a ratio of 1:100. The potassium fixed was extracted in the first two extractions in all cases except for the Middlehurst silt loam where 1.8 me K % had been fixed. The "constant rate" potassium was not affected (see Table 40).

TABLE 40

POTASSIUM SOLUBLE IN NORMAL NITRIC ACID FOLLOWING FIXATION OF POTASSIUM FROM ADDITION OF 5 me K %.

Soil to acid ratio 1:100.

Soil	Exch. K after fixation	Extract number 1	2	3	4	"Step" K after fixation	"Step" K no fixation
	me%	me%	me%	me%	me%	me%	me%
New Plymouth sandy loam	6.00	0.33	0.25	0.24	0.25	0.08	0.08
Taupo sand	5.35	0.42	0.20	0.18	0.16	0.26	0.15
Kiripaka clay loam	6.25	0.63	0.22	0.19	0.18	0.45	0.2
Middlehurst silt loam	3.70	5.45	1.62	1.08	0.94	5.3	3.7
Tokomaru fine sandy loam	4.70	1.40	0.73	0.57	0.59	1.0	0.4
Omakere clay loam	5.00	2.50	1.35	0.93	0.91	2.0	1.4
Idaburn fine sandy loam	5.25	2.98	1.22	0.95	0.92	2.3	2.0
Timaru silt loam	4.30	2.40	0.92	0.90	0.89	1.6	0.7
Halcombe silt loam	4.70	2.41	1.04	0.78	0.80	1.9	1.3
Matamau silt loam	4.95	1.15	0.49	0.45	0.42	0.8	0.2
Waipara silt loam	4.95	3.44	1.36	1.31	1.07	2.8	2.1
Himatangi coarse sand	5.20	1.09	0.77	0.70	0.67	0.5	0.4

POTASSIUM RELEASE ON WETTING AND DRYING AT 105°C

The wetting and drying of soils, instead of producing fixation of potassium, may bring about the release of nonexchangeable potassium. Evans and Simon (1949) used this property in their suggested method for estimating potassium availability. Tested on some of the soils used in this study for cropping, 2 wetting and drying cycles with extraction of exchangeable potassium each cycle, brought about small releases of potassium to the dilute acid. In all cases the release per cycle was small, less than 0.25 me K %. A similar cycle carried out on 3 soil samples which had been extracted once with N HNO_3 to remove "step" potassium, released no potassium from any soil (Table 41).

TABLE 41

NONEXCHANGEABLE POTASSIUM RELEASED ON WETTING AND DRYING AT 105°C

Soil	Exch. K	K released per cycle	
		1	2
	me%	me%	me%
New Plymouth sandy loam	1.10	0.08	0.04
Middlehurst silt loam	0.61	0.24	0.15
Tokomaru fine sandy loam	0.61	0.14	0.10
Omakere clay loam	0.68	0.10	0.10
Timaru silt loam	0.30	0.22	0.06
After one extraction at 1:100 with N HNO_3.			
New Plymouth sandy loam		0.00	
Omakere clay loam		0.01	
Timaru silt loam		0.00	

It is highly probable therefore that the potassium estimated by Evans and Simon is some part of the "Step" potassium. The data presented in their paper, on inspection, would appear to fit a rate of extraction, which rather than being constant, decreased steadily, indicating that a finite amount of potassium was being extracted. An approximation of this amount could be made by extrapolation to approximately 10 cycles.

THE EFFECT OF CROPPING ON ACID SOLUBLE POTASSIUM

It was shown earlier (page 55, and Table 15) that non-exchangeable potassium was used by ryegrass plants while growing for periods of 15 months to 30 months under glasshouse conditions.

Certain of the samples of the soils used for cropping and on which the exchangeable potassium had been determined, were extracted with N HNO_3. The results of these extractions are reported in Tables 42 and 43.

The first series of extractions on the soils, New Plymouth sandy loam, Taupo sand, Kiripaka clay loam, Middlehurst silt loam, Tokomaru fine sandy loam and Omakere clay loam, were carried out at a soil to acid ratio of 1:12½. The remaining two series of extractions were carried out at the soil to acid ratio of 1:100.

TABLE 42

POTASSIUM SOLUBLE IN NORMAL NITRIC ACID FROM POT SOIL SAMPLES

Ratio of soil to acid 1:12½

Soil	Date	Exch. K	Extract Number 1	2	3	4	5
		me%	me%	me%	me%	me%	me%
New Plymouth sandy loam	Initial	1.10	0.24	0.21	0.20	0.20	0.19
	8.3.54.	0.36	0.23	0.24	0.22	0.21	0.21
Taupo sand	Initial	0.46	0.20	0.12	0.09	0.09	0.09
	8.3.54.	0.11	0.20	0.14	0.11	0.13	0.13
Kiripaka clay loam	Initial	1.56	0.29	0.15	0.14	0.14	0.15
	8.3.54.	0.24	0.37	0.13	0.14	0.15	0.14
Middlehurst silt loam	Initial	0.61	3.00	1.46	0.75	0.60	0.49
	8.3.54.	0.35	2.54	1.12	0.75	0.60	0.50
Tokomaru fine sandy loam	Initial	0.60	0.51	0.33	0.27	0.27	0.30
	8.3.54.	0.17	0.50	0.34	0.28	0.31	0.29
Omakere clay loam	Initial	0.68	1.16	0.52	0.46	0.43	0.43
	8.3.54.	0.24	1.01	0.45	0.45	0.40	0.39

Initial dates - see Table 12, page 53.

For all except the Idaburn fine sandy loam, the initial acid extraction of the cropped soils released less potassium than from the uncropped soils. Any variation found between subsequent extractions before and after cropping were not significant and were within experimental error.

Table 44 shows the "step" potassium for each extraction, the change in "step" potassium during the period of cropping, and the non-exchangeable potassium removed by cropping.

A close relationship is seen to exist between the nonexchangeable potassium taken up by the ryegrass and the change in "step" potassium. There was no observable consistent difference in the "constant rate" potassium for any soil.

TABLE 43

POTASSIUM SOLUBLE IN NORMAL NITRIC ACID FROM POT SAMPLES

Ratio of soil to acid 1:100.

Soil	Date	Exch. K	Extract Number			
			1	2	3	4
		me%	me%	me%	me%	me%
New Plymouth sandy loam	Initial	1.10	0.31	0.25	0.28	0.25
	14.12.54	0.16	0.29	0.26	0.26	0.24
	10. 8.55	0.23	0.23	0.24	0.22	0.23
Taupo sand	Initial	0.46	0.32	0.18	0.16	0.15
	14.12.54	0.15	0.26	0.19	0.17	0.18
	10. 8.55	0.16	0.22	0.20	0.17	0.19
Kiripaka clay loam	Initial	1.56	0.37	0.22	0.18	0.17
	14.12.54	0.25	0.28	0.19	0.17	0.19
	10. 8.55	0.16	0.17	0.18	0.17	0.18
Middlehurst silt loam < 2mm.	Initial	0.61	4.33	1.17	0.99	0.94
	14.12.54	0.34	3.49	1.05	0.93	0.92
	10. 8.55	0.48	3.27	1.18	0.96	0.93
Tokomaru fine sandy loam	Initial	0.61	0.87	0.65	0.59	0.57
	14.12.54	0.11	0.75	0.65	0.59	0.52
	10. 8.55	0.12	0.78	0.60	0.56	0.52
Omakere clay loam	Initial	0.68	2.12	1.10	0.91	0.91
	14.12.54	0.18	1.77	1.09	0.95	0.90
	10. 8.55	0.27	1.65	0.93	0.90	0.90
Idaburn fine sandy loam	Initial	0.65	2.76	1.10	0.93	0.94
	14.12.54	0.51	2.82	1.12	0.93	0.90
	10. 8.55	0.56	2.78	1.08	0.90	0.89
Timaru silt loam	Initial	0.30	1.55	0.90	0.93	0.88
	14.12.54	0.22	1.39	0.98	0.91	0.86
	10. 8.55	0.36	1.30	0.88	0.88	0.89
Halcombe silt loam	Initial	0.52	1.82	0.94	0.82	0.78
	14.12.54	0.23	1.75	0.97	0.85	0.82
	10. 8.55	0.25	1.74	1.00	0.88	0.84
Matamau silt loam	Initial	0.55	0.59	0.41	0.42	0.42
	14.12.54	0.39	0.46	0.46	0.42	0.46
	10. 8.55	0.26	0.41	0.40	0.40	0.42
Waipara silt loam	Initial	0.85	2.87	1.28	1.16	1.08
	14.12.54	0.34	2.65	1.25	1.10	1.04
	10. 8.55	0.40	2.51	1.17	1.09	1.02
Himatangi coarse sand	Initial	0.30	1.01	0.80	0.69	0.69
	14.12.54	0.20	0.82	0.79	0.71	0.69
	10.8. 55	0.16	0.82	0.80	0.70	0.68

Initial dates - see Table 12, page 53.

TABLE 44

RELATIONSHIP BETWEEN "STEP" POTASSIUM AND NONEXCHANGEABLE POTASSIUM TAKEN UP BY RYEGRASS

Soil	Date	"Step" K	Change in "Step" K	Nonexch. K taken up
		me%	me%	me%
New Plymouth sandy loam	Initial	0.05	0.0	0.0
	8. 3.54	0.02	0.03	-0.03
	14.12.54	0.03	0.02	-0.03
	10. 8.55	0.00	0.05	0.07
Taupo sand	Initial	0.18	0.0	0.0
	8. 3.54	0.10	0.08	0.01
	14.12.54	0.10	0.08	0.04
	10. 8.55	0.03	0.15	0.07
Kiripaka clay loam	Initial	0.20	0.0	0.0
	8. 3.54	0.22	-0.02	0.02
	14.12.54	0.10	0.10	0.11
	10. 8.55	0.00	0.20	0.19
Middlehurst silt loam < 2mm.	Initial	3.7	0.0	0.0
	8.3. 54	2.7	1.0	1.03
	14.12.54	2.6	1.1	1.23
	10. 8.55	2.5	1.2	1.69
Tokomaru fine sandy loam	Initial	0.4	0.0	0.0
	8. 3.54	0.25	0.15	0.12
	14.12.54	0.30	0.10	0.14
	10. 8.55	0.25	0.15	0.20
Omakere clay loam	Initial	1.4(0.85)	0.0	0.0
	8. 3.54	(0.6)	0.25	0.26
	14.12.54	1.0	0.4	0.43
	10. 8.55	0.75	0.65	0.65
Idaburn fine sandy loam	Initial	2.0	0.0	0.0
	14.12.54	2.0	0.0	0.04
	10. 8.55	1.9	0.1	0.09
Timaru silt loam	Initial	0.7	0.0	0.0
	14.12.54	0.5	0.2	0.20
	10. 8.55	0.4	0.3	0.38
Halcombe silt loam	Initial	1.3	0.0	0.0
	14.12.54	1.2	0.1	0.04
	10. 8.55	1.1	0.2	0.18
Matamau silt loam	Initial	0.2	0.0	0.0
	14.12.54	0.0	0.2	0.11
	10. 8.55	0.0	0.2	0.18
Waipara silt loam	Initial	2.1	0.0	0.0
	14.12.54	1.8	0.3	0.40
	10. 8.55	1.6	0.5	0.64
Himatangi coarse sand	Initial	0.4	0.0	0.0
	14.12.54	0.2	0.2	0.19
	10. 8.55	0.2	0.2	0.20

Initial dates - see Table 12, page 53.

Ratio of soil to acid 1:100 except for analyses dated 8.3.54. and in brackets for Omakere clay loam when 1:12½.

The "step" potassium, although independent of the method of estimation, is seen to be influenced by the level of cropping. Where the "step potassium was reduced to nearly zero by cropping, the percentage of potassium in the dry tissue fell to very low levels and potassium deficiency symptoms became pronounced. Where the "step" potassium was higher, 0.4 me K % or more, the potassium level in the dry tissue was 1% K or more.

IDENTIFICATION OF SOURCE OF AVAILABLE NONEXCHANGEABLE POTASSIUM

The two soils, which showed the greatest change in "step" potassium on cropping, viz. the Middlehurst silt loam and the Omakere clay loam, were fractionated into coarse sand, fine sand, silt and clay by Method B (page 27). Samples of these separates were extracted with $\underline{N}$ HNO_3 at a ratio of 1:100 for the sands and silts and 1:200 for the clays. There was virtually no difference between the mechanical analyses before and after cropping, as shown in Table 45. The extraction data for the texture separates is given in Table 46 showing that with the exception of the coarse sand fraction, potassium was extracted by the ryegrass from each of the fractions from the Middlehurst silt loam. Most of the potassium extracted came from the clay although appreciable amounts came from the silt. For the Omakere clay loam, most of the potassium extracted came from the clay fraction, with a small amount from the silt.

TABLE 45

MECHANICAL ANALYSES, BEFORE AND AFTER CROPPING

Soil		Coarse sand	Fine sand	Silt	Clay	O.M., Loss on $sol^{\underline{n}}$.
Middlehurst silt loam < 2mm.	Before	15.9	32.8	22.2	20.6	9
	After	17.8	32.2	20.1	20.7	9
Omakere clay loam	Before	1.8	23.2	32.5	32.7	10
	After	2.0	22.9	32.4	33.9	10

Because of the considerable influence of deferration on the mechanical analysis and on the distribution of potassium extracted from the Middlehurst silt loam texture fractions, a further sample of Middlehurst silt loam, taken after cropping for 2 years, was treated with 6% H_2O_2 to destroy organic matter, dispersed with calgon and sodium carbonate and the clay separated. The 3 larger fractions were then deferrated by trituration with detergents (details of method, see page 30) and separated by sedimentation into coarse sand, fine sand, silt and clay, the mechanical analysis being shown in Table 47. The separates prepared thus were extracted with N HNO_3. The results of these extractions are given in Table 48, together with the data quoted in Table 27 for the potassium soluble in N HNO_3 from deferrated Middlehurst silt loam texture fractions.

TABLE 48

POTASSIUM EXTRACTED BY NORMAL NITRIC ACID FROM TEXTURE FRACTIONS BEFORE AND AFTER CROPPING

Soil	Ratio		Extract Number 1	2	3	4
Middlehurst silt loam,			me%	me%	me%	me%
Coarse sand	1:12½	Before	1.59	0.73	0.21	0.19
	1:100	After	1.30	0.81	0.40	0.42
Fine sand	1:100	Before	3.01	0.98	0.97	0.95
	1:100	After	2.60	1.12	0.99	0.97
Silt	1:100	Before	4.80	1.57	1.34	1.31
	1:100	After	3.81	1.57	1.33	1.28
Clay	1:200	Before	11.7	2.98	1.99	1.78
	1:200	After	5.5	2.36	1.93	1.82
Omakere clay loam,						
Fine sand	1:100	Before	0.60	0.45	0.39	0.36
	1:100	After	0.65	0.50	0.42	0.42
Silt	1:100	Before	1.47	1.20	1.01	0.87
	1:100	After	1.43	1.10	1.07	0.93
Clay	1:200	Before	5.23	3.28	3.02	2.72
	1:200	After	4.6	2.85	2.87	2.78

These show that instead of potassium being extracted from the sand and finer fractions by the ryegrass, nearly all (> 90%) of the potassium was taken up from the clay with virtually none from the sand fractions. Thus for both the Omakere clay loam and the Middlehurst silt loam, virtually all the potassium taken up by the ryegrass in 2 years cropping came from the clay fraction. It is probable that potassium taken up from the other soils also came from their clay fractions and not from the coarser fractions.

CLASSIFICATION OF SOILS INTO POTASSIUM RESPONSIVE AND NON-RESPONSIVE GROUPS

In the cropping experiment carried out to find the effect of cropping on soil potassium, it was found that the only potassium other than exchangeable potassium, available to ryegrass in 15 months to 2 years cropping, was the "step" potassium (pages 93-96), little or no "constant rate" potassium being used. If the same relationship between potassium available to plants, "step" potassium and "constant rate" potassium exists under field conditions as in the glasshouse, then the determination of the "step" potassium of a soil should give a reliable estimate of its available non-exchangeable potassium. Unless the rate of weathering under field conditions is sufficiently faster than that occurring under glasshouse conditions so that enough available potassium is liberated from other than

TABLE 47

MECHANICAL ANALYSES OF DEFERRATED MIDDLEHURST SILT LOAM

	Coarse sand	Fine sand	Silt	Clay
Before cropping	8.4	28.2	28.6	24.0
After cropping	8.2	28.0	28.9	23.8

TABLE 48

POTASSIUM EXTRACTED BY NITRIC ACID FROM DEFERRATED TEXTURE FRACTIONS OF MIDDLEHURST SILT LOAM BEFORE AND AFTER CROPPING

POTASSIUM EXTRACTED BY NORMAL NITRIC ACID

Soil	Ratio		Extract Number					
			1	2	3	4	5	
Coarse sand	1:12½	Before	0.43	0.19	0.16	0.17	0.16	[illegible]
	1:12½	After	0.45	0.18	0.19	0.17	0.19	[illegible]
Fine sand	1:100	Before	2.00	0.97	0.88	0.90	0.91	
	1:100	After	1.94	0.98	0.88	0.92	0.90	
Silt	1:100	Before	4.50	1.50	1.29	1.25	1.30	
	1:100	After	3.98	1.57	1.33	1.28	1.27	
Clay	1:200	Before	11.5	3.12	2.04	1.81	1.77	[illegible]
	1:200	After	5.7	3.06	1.88	1.75	1.70	[illegible]

"step" potassium - an unlikely premise under New Zealand conditions - then soils without or with low "step" potassium should show potassium deficiencies and responses when the exchangeable potassium is exhausted.

A survey carried out on 39 soils, the potassium status of which was known from the results of trials carried out by the Department of Agriculture (During, personal communication) showed (Table 49) that all soils known to be potassium responsive have a "step" potassium of 0.3 me K % or less, except the very coarse textured Himatangi coarse sand, which has a "step" potassium of 0.4 me K %. The 3 soils tested on which slight responses have been shown, had "step" potassium of 0.3 - 0.4 me K %. Soils known to be not responsive of potassium or on which potassium responses have not been reported, all had "step" potassium of 0.5 me K % or larger.

The range of "constant rate" potassium was from 0.02 - 0.70 me K % for potassium responsive soils and from 0.37 - 1.3 me K % for non-responsive soils. As the ranges overlap considerably, the "constant rate" potassium would not be as good an index for classifying soils as the "step" potassium.

TABLE 49

NORMAL NITRIC ACID SOLUBLE POTASSIUM FROM SOILS OF KNOWN POTASSIUM RESPONSE

Soil and Genetic soil group		Exch. K	Extract Number 1	2	3	4	"Step" K	"Const. rate" K	(a)	K status
		me%	me%	me%	me%	me%	me%	me%	me%	
Wharekohe sandy loam	7b	0.15	0.09	0.06	0.05	0.04	0.0	0.05	0.09	Def.
Wharekohe Silt loam	7b	0.14	0.24	0.22	0.25	0.26	0.0	0.25		Def.
New Plymouth sandy loam	14a	1.09	0.31	0.25	0.26	0.25	0.05	0.25	0.27	Def.
Stratford sand	14d	0.54	0.29	0.28	0.29	0.30	0.0	0.29		Def.
Inglewood coarse sandy loam	14d	0.56	0.36	0.30	0.32	0.32	0.0	0.32		Def.
Takapau silt loam	14a	0.12	0.27	0.29	0.32	0.31	0.0	0.31	0.23	Def.
Karaka complex	14a	0.61	0.38	0.37	0.38	0.37	0.0	0.37		Def.
Rukuhia peat	19	1.20	0.12	0.02	0.01	0.03	0.1	0.02		Def.
Waiuta fine sandy loam	7a	0.31	0.23	0.14	0.17	0.18	0.1	0.17	0.21	Def.
Awahou loamy sand	12	0.25	0.78	0.72	0.71	0.70	0.1	0.70	0.62	Def.
Te Kopuru sand	14a	0.38	0.20	0.08	0.04	0.06	0.15	0.05		Def.
Taupo sand	13a	0.45	0.32	0.18	0.16	0.15	0.2	0.15		Def.
Kiripaka clay loam	16a	1.57	0.37	0.22	0.18	0.17	0.2	0.18		Def.
Hamama stony silt loam	8	0.43	0.35	0.18	0.19	0.22	0.2	0.19	0.30	Def.
Waikiwi silt loam	5B	0.58	0.45	0.32	0.29	0.28	0.2	0.29		Def.
Ohaupo silt loam	14a	1.42	0.55	0.34	0.37	0.37	0.2	0.37		Def.
Owaka silt loam	5B	0.70	0.76	0.56	0.57	0.58	0.2	0.57	0.58	Def.
Marua clay loam	6c	0.22	0.48	0.25	0.21	0.21	0.3	0.21	0.24	Slight
Te Kowhai silt loam	14a	0.45	1.00	0.73	0.77	0.75	0.3	0.75		Slight
Tokomaru fine sandy loam	2f	0.61	0.87	0.65	0.59	0.57	0.4	0.57	0.42	Slight
Himatangi coarse sand	12	0.30	1.01	0.80	0.69	0.69	0.4	0.69	0.58	Def.
Timaru silt loam	2c	0.30	1.55	0.90	0.93	0.88	0.7	0.88	0.75	Not.
Hamilton clay loam	15b	1.94	1.06	0.46	0.37	0.36	0.8	0.37		Not.
Lismore silt loam	2a	0.93	1.68	1.17	0.92	0.98	0.9	0.98		Not.
Halcombe silt loam	2g	0.52	1.82	0.94	0.82	0.78	1.2	0.77		Not.
Omakere clay loam	5b	0.68	2.12	1.10	0.91	0.91	1.4	0.90	0.85	Not.
Waipara silt loam	2b	0.65	2.87	1.28	1.16	1.08	2.1	1.07		Not.
Temuka silt loam	2c	1.64	3.35	1.53	1.20	1.23	2.5	1.22		Not.
Hastings clay loam	2b	1.18	3.41	1.76	1.35	1.28	2.6	1.3		Not.

(a) Extracted at ratio 1:12½, exchangeable potassium not removed prior to extraction, but deducted to give data in column (a).

The relationship between the "step" potassium, "constant rate" potassium and plant response, is shown in Figure 18. It is seen that by placing the soils into groups with "step" potassium figures of less than 0.3 me K %, 0.3 - 0.4 me K %, and 0.5 me K % or more, the soils fall into groups which are potassium deficient and non-responsive with a small group in between. This group, with "step" potassium figures of 0.3 - 0.4 me K %, includes one deficient soil and 3 which show slight responses. The deficient soil is of coarse sandy texture, whereas the others are a clay loam, a silt loam and a fine sandy loam. It is probable that if the potassium status was known for more soils with "step" potassium in the range 0.3 - 0.6 me K %, a more exact relationship between the "step" potassium, texture and potassium status could be derived.

FIGURE 18

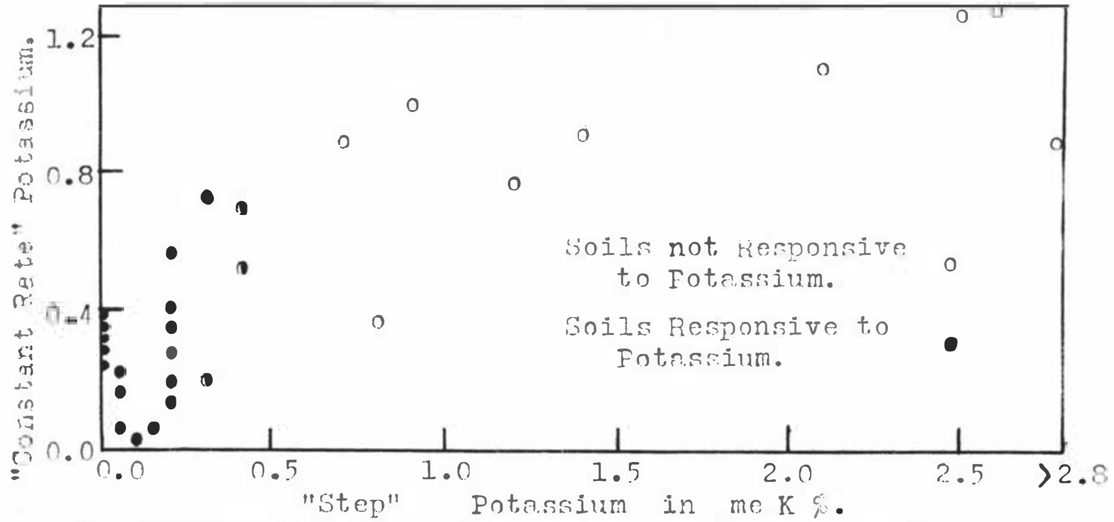


Fig. 18 - Relationship between "step" potassium, "constant rate" potassium and potassium response.

When correlating field responses to potassium with laboratory data, it is essential that no factor other than the level of available potassium controlled the growth rate. Because of the widespread phosphate deficiency in New Zealand, in many of the earlier field trials, the low available phosphate level was the controlling factor in plant growth and misleading negative field responses to potassium were reported. According to During (pers. communication), potassium responses are now being reported in areas, previously considered non-responsive, in which farming has become more intensive and where phosphatic fertilising has become more prevalent. The classification of New Zealand soils into potassium responsive, slightly responsive and non-responsive groups, as shown in Figure 1, is therefore only tentative and will no doubt be modified considerably as farming becomes more intensive and as other nutritional deficiencies are satisfied.

The relationship between "step" potassium and the potassium status is summarized in Table 50. Where farming is very intensive or where crops have particularly high potassium requirements, e.g. lucerne leys, potato and clover seed and hay stands, higher "step" potassium may be necessary to get optimum yields. An example of this has been found in Canterbury where lucerne grown on Lismore silt loam, shallow phase on gravel, with "step" potassium of 0.9 me K %, has shown responses to potassium after 5 years of intensive growth with irrigation.

TABLE 50

RELATIONSHIP BETWEEN "STEP" POTASSIUM AND POTASSIUM STATUS

"Step" potassium.	Potassium status.
< 0.3 me K %	Potassium deficient when exchangeable potassium exhausted.
0.3 - 0.4 me K %	Slight responses to potassium, but potassium responsive if cropped intensively or if of coarse texture.
> 0.5 me K %	Not responsive to potassium.

The initial acid soluble potassium figure at a soil to acid ratio of 1:100 for potassium responsive soils varied from 0.09 - 1.01 me K % and for non-responsive or slightly responsive soils, from 0.48 - 4.3 me K % with all except two soils above 1.05 me K %. This single determination would give almost as good a separation of soils as the multiple extraction method.

As a method for determining potassium responsive soils or soils which will become potassium responsive when the exchangeable potassium is depleted, the determination of the "step" potassium by multiple extraction gives a better indication than the single extraction. The method recommended by Reitemeier et al (1948) and Pratt (1952), i.e the extraction of the soils with $\underline{N}$ HNO_3 at a soil to acid ratio of 1:12½ without prior removal of exchangeable potassium, did not give results of an accuracy comparable with either of the above methods, although on the basis of the 12 analyses reported in Table 49, a division of soils into deficient and not responsive soils could be made at about 0.6 - 0.7 me K %. On the basis of the survey of New Zealand soils using the method of Pratt (1951) not reported here, it appears that this division is not very precise, as although for no deficient soil, the first extraction figure was greater than 0.7 me K %, for several non-deficient soils, it was 0.4 - 0.6 me K %. This limit of $\underline{N}$ HNO_3 soluble potassium in potassium deficient soils is the same as that found by Legg and Beacher (1952) for Arkansas soils.

The method recommended for the most exact classification of soils into potassium deficient and non-deficient groups is as follows.

1. Extract the exchangeable potassium with dilute ($\underline{N}/10$) HNO_3.
2. Extract the hydrogen saturated residue 4 times with $\underline{N}$ HNO_3 by boiling for 15 minutes at a soil to acid ratio of 1:100, the acid added boiling.
3. Calculate the "step" potassium and from Table 50 determine whether potassium deficiency and response is likely.

An alternative method for a division into potassium responsive and non-responsive soils would be

1. Extract the exchangeable potassium with dilute HNO_3.
2. Extract the hydrogen saturated residue once with N HNO_3 by boiling for 15 minutes at a soil to acid ratio of 1:100, the acid added boiling.

If the acid soluble nonexchangeable potassium is less than 0.8 me K %, potassium deficiencies may be expected, if greater than 1.0 me K %, potassium responses are not likely, if from 0.8 - 1.0 me K %, estimate the "step" potassium and apply the rules for correlating "step" potassium and potassium response.

Although when applied to virgin soils, the single extraction method gives quite good separations into potassium deficient and non-deficient soils, when applied to cropped soils, (see Tables 42 and 43), it does not give much indication of the available potassium remaining in the soil. The multiple extraction method with the determination of the "step" potassium gives more information about the amount of available potassium present in the soil.

GENERAL DISCUSSION

As shown by many workers (see Table 2 and pages 10 to 14) potassium other than exchangeable potassium, is available to plants, the amounts varying considerably between soils. In this study, the above findings were confirmed, the proportion of the total potassium taken up by plants, which was non-exchangeable at the beginning of the experiment, varying from 9% to 94%. When Italian ryegrass was grown for 15 months to 2½ years, the uptake of non-exchangeable potassium was up to 1.76 me K %, a figure higher than any published uptake, the previous highest uptake recorded being 1.5 me K % in 42 months for a Hawaiian soil (Ayres, 1949). The uptake for the majority of the soils was from 0.1 - 0.2 me K % with an overall average of 0.35 me K % in 20 months, which is similar to the average of the published uptakes of approximately 0.3 me K % in 2 years, again with a large proportion in the range 0.1 - 0.2 me K %. It would appear that New Zealand soils are similar to the soils of the U.S.A. in the availability of non-exchangeable potassium.

The initial exchangeable potassium was found to be a poor indicator of the total potassium available. For example, with soils of higher than average potassium supplying power, the exchangeable potassium, at 0.5 - 0.6 me K %, was little different from that of other soils. When the initial exchangeable potassium level is low, the non-exchangeable potassium is of greater relative importance as a source of available potassium than when the exchangeable potassium is high. From the published information consulted, it appears that the general level of exchangeable potassium in the soils of the U.S.A., tends to be about 0.2 - 0.4 me K %, e.g. Lilleland (ref. Williams and Jenny, 1952) in a survey of Californian soils found that 70% of the soils had exchangeable potassium levels of 0.4 me K % or less. Under these conditions, the non-exchangeable potassium must supply a large part of the crop potassium.

The relative contribution of the exchangeable potassium and of the non-exchangeable potassium to the potassium uptake, has been expressed by Schmitz and Pratt (1953) and by Semb and Uhlen (1955) in the form of multiple regression equations. They found that the best correlation between plant uptake and soil potassium was given by the relationship that the uptake of K was 95-100% of the initial exchangeable potassium plus 15 - 20% of the potassium soluble in one extraction with $\underline{N}$ HNO_3 at a soil to acid ratio of 1:12½. For the soils cropped in the course of this study, the above relationship applies approximately for the first year's cropping and less accurately for the second year's cropping for those soils cropped for 2½ years. The correlation was poorest where the acid soluble potassium was very low or very high, the calculated uptake being too high when the acid soluble potassium was very low and too low when the acid soluble potassium was high.

A slightly better correlation between the annual plant potassium uptake and soil potassium was given by the equation

K in crop = 4/5 Initial exch. K + 1/4 "step" K.

The uptake of potassium from the Ideburn fine sandy loam and from the Halcombe silt loam did not fit any suggested relationship between plant uptake and acid soluble and exchangeable potassium.

The source of the nonexchangeable available potassium was shown by Olsen and Shaw (1943) and by Merwin (ref. in Reitemeier, 1952) to be associated largely with the finer texture fractions. This was confirmed in this study, where it was shown that the potassium taken up by the ryegrass came almost entirely from the clay fraction with the remainder from the silt. Extraction with N HNO_3 of the texture separates by Rouse and Bertramson (1950) and by Pratt (1951) showed that on a unit weight basis, most potassium was extracted from the < 2 μ fractions, the amount falling off rapidly with increasing particle size. Rouse and Bertramson found that with soils predominately of sand and silt, half of the acid soluble potassium came from the clay fraction. Pratt, with fairly sandy soils found that the clay contributed from 40-75% of the acid soluble potassium. In this study, the greater solubility of the potassium from the clay fraction was confirmed, Table 24 showing that apart from the two sandy soils, from 40-90% of the acid soluble potassium came from the clay fraction.

Because of the large contribution of the clay fractions to the potassium extracted by N HNO_3, it should be possible to establish relationships between the clay mineral content of the soils and the "step" potassium, the "constant rate" potassium and potassium fixation. Although no tests of the potassium fixing power of the texture fractions were carried out on the New Zealand soils studied, N.J. Volk (1934) and others have shown that the potassium fixing power of soils is a function associated virtually entirely with the clay fraction.

As the exact quantitative clay mineral distribution is not available for the soils studied, any relationships derived must be of a qualitative nature. By grouping the soils according to the genetic classification of Taylor (1948) and by using the information about the clay mineral distribution in the genetic soil groups published by Fieldes et al (1954, 1955), as in Table 51, it may be seen for the Zonal soils that with increasing intensity of weathering, the "step" potassium tends to decrease from approximately 2 me K % found in the brown-grey earths and in the yellow-grey earths to 0 me K% in the podzolized yellow-brown earths.

The brown-grey earths, with the clay mainly weakly hydrated mica, had a high "step" potassium of 2.0 me K % and a medium potassium fixing power of 0.4 me K %. In the yellow-grey earths where more weathering has taken place and illite and clay-vermiculite predominate, the "step" potassium is still high, 0.7-2.6 me K % (average 1.7 me K %). These figures exclude the data for the Tokomaru fine sandy loam, the clay mineral of which, according to Fieldes (personal communication) is illite or possibly a collapsed clay-vermiculite, which as a result of its alluvial origin is low in potassium. The potassium fixing power of the yellow-grey earths is higher than that for the brown-grey earths (0.7-1.0 me K % against 0.4 me K %) but this is probably the result of the higher clay percentages in the yellow-grey earths compared with the brown-grey earth (16-22% against 7½%) rather than from any difference in the clays. In the yellow-brown earths where further weathering has occurred, a considerable decrease in both the "step" potassium and in the potassium fixing power is found even with the much higher clay content (33% for the Omakere clay loam) in these soils. In the podzolized yellow-brown earths, where 2:1 type layer lattice minerals are not found, the "step" potassium is very low, 0.0-0.1 me K %.

The intrazonal soils without layer lattice minerals, viz. the yellow-brown pumice soils, yellow-brown loams, and red-brown loams derived from basalt from Northland, are also low in acid soluble potassiu, both "step" potassium and "constant rate" potassium. These soils do not fix potassium and although often high in exchangeable potassium in the virgin state, become very deficient in available potassium when cropped for some time. Because of their favourable structure and the favourable climate associated with them, farming has been relatively more intensive on these soils and the first potassium responses in New Zealand were observed on soils of these groups.

Two anomalous soils are the red-brown loam, Middlehurst silt loam, and the brown granular clay, Hamilton clay loam. Both have high "step" potassium and high "constant rate" potassium and the Middlehurst silt loam has a very high potassium fixing capacity. The Middlehurst silt loam, although derived from basalt, must contain a considerable amount (up to one half) of non-basaltic material, because examination of the deferrated fine sand shows that the majority of the fraction S.G. < 2.7, which makes up 55% by weight, is quartz and acid felspar. According to Fieldes and Williamson (1955), the clay fraction is largely amorphous although it contains some hydrous mica. Until more is known of the clay minerals in this soil, no explanation of the very high acid solubility of the potassium, the high fixation power and the ready availability of the non-exchangeable potassium, can be given.

The other soil, the Hamilton clay loam, which is derived from old andestic Hamilton ash, has as the dominant clay mineral an unusual tubular form of meta-halloysite (Fieldes and Williamson, 1955). As this mineral is present in the strongly weathered yellow-brown earths, group 6, which are low in acid soluble potassium (see Marua clay loam, Table 49), it is probably not the sole cause of the high potassium extractions data. It is of interest that Allison and Roller (1955)

TABLE 51

RELATIONSHIP BETWEEN GENETIC CLASSIFICATION AND "STEP" POTASSIUM AND POTASSIUM FIXING POWER

Genetic Soil Group		Representative soils	Predominant clay minerals	"Step" K in me %	K fixing power in me % (one cycle)
Zonal Soils					
Brown-grey earth	1	Idaburn f.s.l.	Mica, Il	High 2.0	Med. 0.4
Yellow-grey earth	2	Waipara si.l Hastings c.l. Halcombe si.l. Timaru si.l. Temuka si.l. Tokomaru f.s.l.	Il, Mica, V	Mainly high 0.7-2.0	High 0.7-1.0
Yellow-brown earth, mod. weathered	5	Omakere c.l. Owaka si.l. Waikiwi si.l.	Il.,V,M,Hal.	High 1.4 to Low 0.2	Med. 0.8 — —
Yellow-brown earth	7	Waiuta f.s.l. Wharekohe si.l.	Q,S, Hal.	Very low 0.0-0.1	—
Intrazonal Soils					
Yellow-brown pumice soils	13	Taupo sand	Allo AB,Cl. F	Low 0.2	Very low 0.1
Yellow-brown loam	14	New Plymouth s.l. Takapau si.l. Te Kopuru sand	Allo.A, Hal.	Very low 0.0-0.3	Very low 0.0-0.1
Brown granular clay	15	Hamilton c.l.	Hal.	High 0.8	—
Red-Brown loam	16	Kiripaka c.l.	Gibbsite, Hal. Fe ox,	Low 0.2	Low 0.3
		Middlehurst si.l.	Amorphous hydrous, oxides, H.M., palagonite	Very high 3.7	Very high 1.9

Key to mineral abbreviations ..... Table 32, page 83.

reported that halloysite was able to trap ammonium ions in a form not replaceable by potassium. A similar explanation may be the reason for the high figures found for the Hamilton clay loam.

Summarised, where weakly weathered micas, illite and clay vermiculite predominate, the "step" potassium and potassium fixation are high and no potassium responses are found. Where no 2:1 layer lattice minerals are present, "step" potassium and potassium fixation are low and potassium responses are common.

When Pratt (1951) summed the weighted acid soluble potassium values from the texture fractions, he found that the sum was less than the potassium extracted from the whole soil in all cases, the deficiency being from 4 - 20% (up to 0.54 me K % on 1.98 me K %). He ascribed the differences to losses of potassium during fractionation. This effect was noticed in the extraction of the Specific gravity separates of the fine sand from the Idaburn fine sandy loam (Table 31). Whereas the first extraction at a sand to acid ratio of 1:12½ dissolved 0.84 me K %, the weighted sum of the first extracts of the specific gravity separates was 0.45 me K %. At ratios of 1:250 for the fraction, S.G. $>$ 2.96, 1:600 for the fraction S.G. 2.96 - 2.69, and 1:100 for the fraction S.G. $<$ 2.69, which represented the ratios of fraction to acid when the fine sand was extracted at a ratio of 1:100, the sum was 1.35 me K % compared with the first extract of the fine sand at the ratio of 1:100 of 1.42 me K %. As Pratt extracted all fractions and soils at a constant ratio of 1:12½, the incomplete summation found by him was probably the result of extracting the fractions at ratios different from those at which they would be extracted as part of the whole soil. This would apply particularly to the clay fractions because of the sandy nature of the whole soils.

For the New Zealand soils tested, as can be seen in Table 24, the weighted sum of the "step" potassium and of the "constant rate" potassium was very close to that observed when the soils were extracted at a ratio of 1:100, except for the Himatangi coarse sand where the values used for the coarse sand which comprises 46% of the soil, were those obtained by extraction at the ratio 1:12½. For 4 of the 5 soils where summations were made at the ratio 1:12½, the calculated maximum values of the "constant rate" potassium were much less than the actual "constant rate" potassium.

The importance of extracting under similar experimental conditions, brought out in the above comparisons, was emphasized when the effects of various cations on the potassium extracted was seen. Lack of appreciation of the effect of the ammonium ion on the potassium extracted probably led Reitemeier, Rouse and Bertramson and Pratt to extract their soils without removing exchangeable potassium, even though a figure calculated by difference is subject to twice the error of a directly determined one.

Although the $\underline{N}$ HNO_3 soluble fraction of the soil potassium has been for 15 years the best estimate of the available nonexchangeable potassium, it has given consistently better correlations with potassium uptake at high acid soluble potassium levels than at low levels where the acid tended to remove a greater proportion of nonavailable potassium. On virgin soils, which normally have higher soil potassium than cropped unfertilized soils, a single extraction affords a good indication of the potassium status but when applied to cropped soils to determine the amount of potassium still available, it is not very accurate. A better indication of the potassium availability is given by the form of the graph obtained by plotting the potassium contents of successive acid extracts against the extraction number particularly when cropped soils are examined. The suggestion of Metson and Arbuckle (1953) that the constant rate of extraction which is found in most soils for the 3rd and subsequent extracts, is a better measure of the potassium availability than a single extraction, was not substantiated in this study, the single extraction giving a much more reliable estimate of potassium deficiency. They compared the constant rate of extraction by $\underline{N}$ HNO_3 with that found by Evans and Simon (1950) for cold $\underline{N}/2$ extractions after a heat treatment. It was shown here that the potassium extracted by the method of Evans and Simon was probably part of the "step" potassium not the "constant rate" potassium as determined by Metson and Arbuckle.

The best index of available non-exchangeable potassium appears to be the "step" potassium, i.e. the potassium extracted by $\underline{N}$ HNO_3 in the first extractions at a rate greater than the later constant rate. This "step" potassium was shown to be a definite fraction of the soil potassium of any soil sample, not affected by the conditions of extraction, provided they are kept constant from one extraction to another. It was shown further that it was of clay or weathered particle coating origin and that it was associated essentially with micas and micaceous minerals.

It is suggested that, as the "step" potassium, except where present as biotite or vermiculite, is associated in soils with weathered minerals, it must be a by-product of weathering. Assuming that the theory proposed by Jackson et al (1952) that the weathering of micas proceeded in partially weathered, partially expanded planes in preference to the initiation of weathering in an unweathered unexpanded plane, is correct and also that in any soil, a definite proportion of the planes are partially weathered, then the "step" potassium might well be the potassium remaining in partially expanded planes. Being partially expanded, hydrogen ions would find ready access into these planes. Further, because of changes in the partially weathered planes brought about by hydration of the lattice, it is reasonable to assume that potassium and ammonium ions would not be able to collapse the lattice in the partially weathered planes to any great extent unless present in large amounts, but would have a much stronger effect on the unweathered planes. If the "constant rate" potassium represents the rate of attack on the unweathered and unexpanded planes, the above hypothesis would provide a reasonable explanation of the effect of potassium and ammonium on the "constant rate" potassium and of the independence of the "step" potassium of these ions. It is considered that the "constant rate" potassium also includes the potassium resulting from the solution of felspars. The constancy of the rate of extraction from orthoclase implies that the extraction of potassium does not become more difficult as the extraction proceeds, i.e. the action of $\underline{N}$ HNO_3 is one of solution of the felspars as a whole rather than extraction of potassium from the inside of the framework which is left unchanged.

Other properties of the "step" potassium are consistent with the hypothesis advanced above, e.g.

1. The reduction of the "step" potassium under intensive cropping would be the result of extraction of some of the potassium from partially weathered planes at a rate faster than weathering was initiated in fresh unweathered planes.
2. The slow increase in "step" potassium under fallow or low rates of cropping, some indication of which was shown by the Middlehurst silt loam during the latter stages of cropping, would be the result of further planes becoming partially weathered.
3. The increase in "step" potassium when potassium is fixed, would follow if potassium were fixed in the partially weathered planes from which it would be readily extractable by $\underline{N}$ HNO_3 to appear as "step" potassium.

SUMMARY

An investigation was carried out into the availability of non-exchangeable potassium, using soils the mineralogical content of which was known for the clay and fine sand fractions.

Before work involving potassium determinations was possible, it was necessary to have an exact method for the estimation of potassium. Estimation by flame photometry was decided on as the best method because of the speed, accuracy and specificity of this method. Following a critical examination of the conditions essential for maximum accuracy, a flame photometer was designed and constructed.

The soil potassium was fractionated into exchangeable potassium and non-exchangeable potassium, the non-exchangeable potassium being fractionated further into acid soluble potassium and acid insoluble potassium.

The exchangeable potassium was estimated by extraction with dilute nitric acid or with neutral normal ammonium acetate and the non-exchangeable potassium fractionated by extraction with normal nitric acid.

Nitric acid was shown to extract considerable amounts of non-exchangeable potassium from the soil samples tested, the amount extracted being governed by

a. The time of heating. The amount of potassium extracted was shown to increase with time up to 10 minutes after which for some soils the rate of increase fell sharply.

b. The acid concentration, but not within the range N/2 - 2 N.

c. The ratio of soil to acid. In general, more potassium was extracted with widening ratios with, for most soils, a ratio beyond which no further increase was found in the potassium extracted. Where the potassium was extracted by leaching with acid, the effect of varying the rate of leaching was comparable with that of altering the soil to acid ratio in the batch extraction.

d. The presence of cations, ammonium and potassium. Both were found to depress the amount of potassium extracted by acid, e.g. exchangeable potassium, if not removed, depresses the amount of potassium extracted in the first extraction with acid for many soils. A similar effect was found if ammonium acetate was used to remove exchangeable potassium, the exchangeable ammonium or any excess ammonium from the acetate, depressing the first potassium extraction figure.

e. The type of extraction, whether by continuous leaching or by single or by multiple batch extraction. A comparison of these methods of extraction showed that multiple batch extraction possessed certain advantages over the other methods, viz.

  i. With the leaching method, it gave a fuller picture of the acid

soluble potassium than that from a single extraction.

ii. Batch extraction gave exact control of the soil to acid ratio.

iii. The case of leaching of the acid through the disc of soil, which limits the range of extraction conditions with leaching extractions, is not a factor in the control of batch extractions.

iv. A much wider range of soil to acid ratios is possible with batch extraction.

When soils were extracted by the multiple batch extraction method, the form of the graph obtained when the amount of potassium extracted is plotted against the extraction number is that of a constant level, preceded by one or more steps above it. The constant level of extraction was assumed to represent the rate of solution of the less soluble forms of potassium and the steps above this level, the amount of a more soluble form of potassium. These forms were called "Constant Rate" potassium and "Step" potassium respectively. The "step" potassium was shown to be independent of the conditions of extraction a - e, but the "constant rate" potassium was found to be dependent on the above conditions.

To identify the texture fractions which are the source of the "step" potassium and of the "constant rate" potassium, sand, silt and clay fractions separated from the soils used for the glasshouse cropping experiment carried out in this study, were extracted with N HNO_3. These extractions showed that the majority of the acid soluble potassium was extracted from the clay fraction, both on a unit weight basis and on a weighted contribution basis, the proportions of the "step" potassium and of the "constant rate" potassium of the whole soil, coming from the clay fraction, varying from 44% to 95% for loams and 11% to 24% for sands for the "step" potassium and from 20% to 71% for loams and 3% for sands for the "constant rate" potassium.

Extraction of typical potassium containing minerals, muscovite, biotite, vermiculite and orthoclase, ground to sand and to silt size, with N HNO_3 after removal of any exchangeable potassium liberated during grinding and of samples of the clay minerals, illite, kaolinite and montmorillonite without grinding, showed that the "step" potassium and the "constant rate" potassium contents were as follows - illite and muscovite, both "step" potassium and "constant rate" potassium, biotite and vermiculite, "step" potassium only, kaolinite and montmorillonite, neither "step" potassium nor "constant rate" potassium. As about 90% of the "step" potassium came from the clay fraction, it was assumed that illite was the main source of soil "step" potassium.

A reasonable correlation was obtained between the distribution of illite and similar clay minerals in the genetic classification soil groups and the "step" potassium of those groups.

An hypothesis regarding the nature of the "step" potassium and the "constant rate" potassium was advanced, the "step" potassium from the clay fraction being postulated as that potassium occurring in the partially expanded planes in the clay minerals, illite, clay vermiculite and hydrous mica intermediates. The "step" potassium from the coarser fraction was regarded as coming from the micas. The "constant rate" potassium was considered to arise from the acid attack on unexpanded planes in the clay minerals and from solution of the felspars and other potassium containing minerals.

Potassium was shown to be fixed by wetting and drying at 106°C or on moist storage for one week, the potassium fixed being acid soluble and appearing as "step" potassium. The "constant rate" potassium was not affected by fixation.

An investigation into the availability of soil potassium was carried out by cropping 12 soils intensively with Italian ryegrass under glasshouse conditions for 15 months to 2½ years. The effect of the removal of available potassium by cropping on the soil potassium distribution was that both exchangeable and non-exchangeable potassium were used. A rapid fall in the level of exchangeable potassium occurred in all cases when growth was rapid but a slow rise in the exchangeable potassium was found in a few cases when growth became slow during the hot weather. The potassium percentage in the plant tissue was shown to be sensitive to the exchangeable potassium level.

The two forms of acid soluble potassium were affected differently by cropping, the "constant rate" potassium being not affected, but the "step" potassium being reduced, the reduction being equal to the uptake of non-exchangeable potassium. Extraction of the texture fractions of 2 soils after cropping showed that virtually all the available non-exchangeable potassium came from the clay fraction "step" potassium. The available potassium under the conditions of the cropping carried out was "step" potassium. The corollary is that soils with no "step" potassium contain no available non-exchangeable potassium.

A survey of the "step" potassium content was carried out on some New Zealand soils, representing the main soil groups and those soil types known to be potassium responsive. A reliable classification into soils, which are potassium deficient or on which potassium responses have been shown, and into soils which are not potassium deficient was shown to be practicable on the basis of the "step" potassium content of the soils. Soils with "step" potassium contents less than 0.3 me K% were those which were potassium deficient, those with "step" potassium contents from 0.3-0.4 me K% were slightly responsive, but if of coarse texture or if cropped intensively, greater responses were recorded. Those with "step" potassium greater than 0.5 me K% were not potassium deficient.

A method, based on the above conclusions, for classifying soils into responsive and non-responsive groups was proposed.

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