

**RELEASE OF
NON-EXCHANGEABLE POTASSIUM
IN HAWAIIAN SUGAR CANE SOILS**

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ABSTRACT

Studies on the Mainland and in Hawaii have shown that the supply of exchangeable potassium in the soil at the start of a crop does not comprise the entire amount of this nutrient to which the crop has access. Additional potassium is converted from the non-exchangeable to the exchangeable form in the course of the crop. It remained, however, to determine the rates of release of non-exchangeable potassium in the widely varying types of soil cropped to sugar cane and to learn more of the factors influencing the process. A need was felt also for a simple, practical means for measuring the rate of release of potassium.

The rates at which non-exchangeable potassium was liberated were found to depend upon the technique employed. Thus release upon cropping was more rapid than upon moist storage following removal of part or all of the exchangeable potassium. The capacities of the soils to liberate potassium were found to cover a wide range. Release was generally most rapid in the least weathered soils. In numerous cases more of the potassium absorbed by the crops was derived from the non-exchangeable than from the exchangeable form.

Ca-soils liberated potassium upon moist storage more rapidly than H-soils. However, liming of untreated acid soils did not effect the release of potassium.

Levels of exchangeable potassium were depleted rapidly under conditions of intensive cropping. Such depletion was not, however, necessary to the utilization by the plants of large amounts of non-exchangeable potassium.

Some promise was obtained that techniques more rapid than the conventional methods might be employed for the measurement of rates of release of potassium.

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By

A. S. AYRES²

SUGAR CANE, the major economic crop of the Hawaiian Islands, requires large quantities of potassium for its development. Moreover, the demand for potassium is continuous since fallowing or resting of the soils is unknown in Hawaiian sugar cane agriculture. The bulk of the potassium contained in the crop at harvest is not returned to the soil, as in the case of many crops, but is largely exported in the form of raw molasses or is lost through burning of the extracted plant residues. Owing to the initially low potassium content of the rock from which the soils are derived and to climatic conditions conducive to rapid weathering and leaching of the potassium minerals, the majority of Island soils are poorly supplied with potassium. As a result, large quantities of potassium fertilizer must be imported and applied each year to maintain soil productivity. In view of these facts, it is desirable to make the best possible use of native potassium already in the soil. A better understanding of the potassium-supplying power of Island soils should prove a step in this direction.

For many years it was believed that the potassium available in the soil to a particular crop consisted of that present in the soil solution and in exchangeable form, together with a practically negligible quantity assumed to be made available as a result of weathering of primary minerals. Although this concept of the potassium-supplying power of the soil probably approximates the true picture in some soils, it is by no means adequate to explain the sustained potassium fertility of others under conditions of continuous cropping.

Martin (37) and Fraps (18) in 1929, Gedroiz (19) in 1931, and Hoagland and Martin (23) in 1933 demonstrated that some soils may release substantial quantities of non-exchangeable potassium to growing crops. Abundant support of this fact has been obtained in more recent years by numerous workers (9, 14, 16, 17, 47, 51, 57). The release of non-exchangeable potassium is not necessarily conditional upon root activity. This has been shown by Bray and De Turk (12) and by Wood and De Turk (59), as well as by Allaway and

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Pierre (2) and York and Rogers (61), who observed varying degrees of release of non-exchangeable potassium upon moist storage of soils following removal of the exchangeable potassium by chemical means. A few workers, among them Abel and Magistad (1) and Bartholomew and Janssen (8), have reported the liberation of potassium from untreated soils either upon moist storage or upon fallowing. Fixed potassium resulting from additions of potassium salts to soils has been released by the same process according to the studies of Bray, De Turk, Wood (16, 59), and others.

Release of non-exchangeable potassium is not a function of temperate zone soils alone. Evidence of release in Hawaiian soils was obtained by Horner (24), who observed in 1930 that a crop of mature pineapple plants contained more potassium per acre than was present in the soil in exchangeable form at the start of the crop, although potassium fertilizer was not added. A subsequent pot study of Hawaiian pineapple soils by Abel and Magistad (1) in 1935 indicated release of non-exchangeable potassium averaging about 100 pounds of K_2O per acre-foot of soil annually when the soils were limed; somewhat less was released by unlimed soils. Release of potassium in a Humic Latosol was suggested by the results of a study of the potassium requirements of sugar cane by Borden (10) in 1941. Subsequently, Ayres (5) reported the conversion of 375 pounds of potassium per acre-foot of soil from the non-exchangeable to the exchangeable form in a Low Humic Latosol coincident with a study of the susceptibility of exchangeable potassium to loss by leaching. A few years later (1946) Ayres, Takahashi, and Kanehiro (6), in a $4\frac{1}{2}$ -year field study with Napier grass, *Pennisetum purpureum*, on a Low Humic Latosol, reported release of non-exchangeable potassium ranging from 3,400 to 4,200 pounds K_2O per acre for the entire period, depending upon the extent of fertilization with nitrogen and phosphorus.

The purpose of the present study was (1) to determine the rates at which release of non-exchangeable potassium occurs in the principal types of sugar cane soils and factors influencing the rate of release, and (2) to find, if possible, a simple, practical means for its measurement.

DESCRIPTION OF SOILS STUDIED

Hawaiian soils have been formed principally from basaltic and, to a much lesser extent, from andesitic lavas and their derivatives. Exceptions consist in agriculturally unimportant peat soils and relatively small areas adjacent to the sea which have been derived in part from calcareous reef rock or coral sand.

Despite the essential chemical uniformity of parent material, extreme diversity exists among the soils of the Islands owing to great differences in geologic age, relief, vegetation, rainfall, and physical state of the parent rock. Vegetation varies from sparse grass in areas of low and seasonal rainfall to dense tropical forests. Rainfall is extremely varied, ranging from 15 inches to 250 inches annually in agricultural areas alone. Volcanic cinders and ash weather far more rapidly and lead to soils of much lower volume weight and of different chemical properties than compact lavas. The dominant soil-forming process is laterization. Hawaiian soils are, for the most part, clay soils, many of them being largely colloidal, but their true physical nature, especially in the case of the residual soils, is not apparent upon casual field observation.

The majority of Hawaiian soils are formed under conditions of substantial rainfall and good drainage, and are generally well weathered. The principal clay mineral in these soils is kaolinite (15). Other soils, including the Gray Hydromorphic Soils, the Alluvial Soils, the Intrazonal Dark Magnesium Clays, and certain of the Low Humic Latosols, are formed under conditions of low rainfall and generally restricted drainage. Some of these soils have been affected in varying degree by ground water which, in some places, has taken the form of seepage from adjacent uplands. Such waters often contain considerable quantities of magnesium which exert a pronounced effect upon the chemical and physical properties of soils through which they move. These soils are relatively little weathered.

The recently completed U.S. Department of Agriculture survey of the soils of the Hawaiian Islands³ reveals the presence of some 16 great soil groups embodying 45 soil families. The latitude in soils devoted to sugar production is evidenced by the fact that 28 of these families are represented on the sugar plantations. The capacities of these soils to produce sugar cover a wide range from 0.20 to 0.50 ton sugar per acre per month,⁴ the most productive being those favored with an abundance of sunshine and adequate irrigation.

Results of the soil survey were not available at the time the bulk of the samples for the present study were taken (1944) and, consequently, the collection is not as representative of the various soil categories cropped to sugar cane as might be desired. Twenty-four samples, representing the sugar cane soils of the four sugar-producing islands, were taken for this study, together with one each from fields of the Experiment Station, Hawaiian Sugar Planters' Association, in Honolulu and the Poamoho Branch Station of the Hawaii Agricultural Experiment Station at Poamoho, Oahu. With the possible exception of some of the Humic Ferruginous Latosols, Hawaiian soils show no evidence of a B-horizon.⁵ Since the entire solum consists of a zone of eluviation, samples were accordingly taken to an arbitrary depth of 1 foot. This depth is generally intermediate between depths of plowing on the unirrigated and irrigated plantations, soils on the latter being plowed more deeply. Samples were collected either from plowed fields, which ordinarily would not have received potassium fertilizer for more than a year, or from fields of young cane. Care was taken to avoid areas to which potassium is usually applied, namely, in the vicinity of the row itself. The samples were air dried, passed through a 2-mm. screen, and stored in covered stone crocks. Some of the chemical properties of the soils are shown in table 1. Further soil specimens were obtained in 1949 for supplementary tests. These were selected from virgin and sugar cane soils and in a manner to be described.

³ U.S.D.A. Hawaii soil survey report. In press.

⁴ *Op. cit.*

⁵ In conformity with common usage, however, the term "B-horizon" is frequently employed in describing Hawaiian soil profiles.

METHODS OF ANALYSIS

Exchangeable cations were extracted from the soil with *N* ammonium acetate adjusted to *pH* 7.0. Calcium in the extracts was determined by precipitation as the oxalate, followed by titration with potassium permanganate. Determination of magnesium was made according to the colorimetric method outlined by Peech (43). The cobaltinitrite method of Volk and Truog (53) for exchangeable potassium, which has proved satisfactory for Island soils containing usual amounts of this element, was found to be insufficiently sensitive for the determination of the very small quantities of potassium encountered in some phases of the study. Gow's (21) colorimetric modification of the chloroplatinate method was employed for a time but was subsequently superseded by the method of Volk (52) which, of the three procedures, was found to be the most satisfactory where the quantity of potassium was small.

TABLE 1. Some Properties of the Soils Studied.

Soil No.	Soil Group	Soil Family	Symbol	Location
44-3	Low Humic Latosol	Lahaina	N2	Makiki, Oahu
44-6	Gray Hydromorphic Soil	Honouliuli	H1	Ewa, Oahu
44-7	Low Humic Latosol	Wahiawa	N3	Waialua, Oahu
44-8	Low Humic Latosol	Wahiawa	N3	Poamoho, Oahu
44-9	Low Humic Latosol	Waimanalo	N7	Waimanalo, Oahu
44-10	Alluvial Soil	Kawaihapai	V1	Wailuku, Maui
44-11	Alluvial Soil	Kawaihapai	V1	Puunene, Maui
44-12	Low Humic Latosol	Lahaina	N2	Lahaina, Maui
44-13	Low Humic Latosol	Lahaina	N2	Paia, Maui
44-14	Low Humic Latosol	Lahaina	N2	Paia, Maui
44-15	Humic Ferruginous Latosol	Puhi	T4	Kilauea, Kauai
44-16	Humic Ferruginous Latosol	Puhi	T4	Kealia, Kauai
44-17	Humic Ferruginous Latosol	Puhi	T4	Lihue, Kauai
44-18	Low Humic Latosol	Kahana	N4	Puhi, Kauai
44-19	Low Humic Latosol	Kohala	N5	Eleele, Kauai
44-20	Low Humic Latosol	Molokai	N1	Makaweli, Kauai
44-21	Intrazonal Dark Magnesium Clay	Lualualei	M	Kekaha, Kauai
44-23	Low Humic Latosol	Kahala	N4	Aiea, Oahu
44-24	Low Humic Latosol	Molokai	N1	Waipahu, Oahu
44-25	Low Humic Latosol	Wahiawa	N3	Waipahu, Oahu
44-26	Hydrol Humic Latosol	Hilo	K6	Olaa, Hawaii
44-27	Hydrol Humic Latosol	Hilo	K6	Olaa, Hawaii
44-28	Humic Latosol	Kapoho	A9	Pahala, Hawaii
44-29	Low Humic Latosol	Kohala	N5	Hawi, Hawaii
44-30	Humic Latosol	Ookala	A5	Paaulo, Hawaii
44-31	Hydrol Humic Latosol	Hilo	K6	Honomu, Hawaii

*Analyses performed in part by H. H. Hagihara.

Cation exchange capacity was determined by leaching the soil with *N* ammonium acetate pH 7.0, washing with 95 percent ethanol, followed by distillation and titration of the adsorbed ammonia. The hydrofluoric acid-sulfuric acid digestion method, using 100-mesh soil, was employed for total potassium. Organic matter was determined by a modification of the Walkley-Black method (54). The glass electrode was employed for the determination of soil reaction.

EXCHANGEABLE AND NON-EXCHANGEABLE FORMS OF POTASSIUM

In a paper devoted to consideration of exchangeable and non-exchangeable forms of soil potassium, it may be in order to consider for a moment what is meant by these terms. Considering the electrostatic nature of the bond by which potassium is held in soil minerals, it is readily conceivable that the reason more

TABLE 1. *Continued.*

Elevation	Mean Annual Rainfall	pH	Exchangeable Cations			Cation Exchange Capacity	Total Potassium (K ₂ O)	Organic Matter
			Potassium	Calcium	Magnesium*			
<i>Feet</i>	<i>Inches</i>		<i>m.e./100</i>	<i>m.e./100</i>	<i>m.e./100</i>	<i>m.e./100</i>	<i>Percent</i>	<i>Percent</i>
50	38	6.9	1.34	23.36	11.14	35.8	0.51	2.80
10	15	7.0	1.00	14.62	12.27	25.6	.40	2.79
400	36	6.5	.49	10.30	5.76	17.7	1.03	3.63
700	45	5.4	.29	5.62	1.54	14.5	1.46	3.40
200	75	6.3	1.34	17.52	11.88	34.6	.45	4.41
250	20	6.6	3.39	19.81	8.51	31.6	.54	3.25
250	20	6.5	1.29	6.27	4.84	14.9	.51	2.34
650	23	5.9	.38	7.40	3.17	15.4	.47	2.57
700	13	6.1	1.63	6.48	3.39	15.1	.38	2.20
150	44	6.1	1.00	6.20	6.20	17.4	.97	3.57
300	67	6.0	.089	9.11	2.00	18.1	.72	6.96
400	39	5.8	.19	7.92	2.86	17.8	.71	6.98
500	75	4.9	.26	3.58	.54	19.3	.38	7.50
375	50	5.9	.32	10.00	3.82	18.4	1.15	5.85
400	60	6.0	.36	8.10	3.19	16.1	.90	5.98
440	30	6.3	.26	8.13	3.64	14.8	.72	4.03
15	20	7.7	.51	77.7	.23	3.09
450	46	6.2	.24	6.30	4.81	12.8	.73	3.77
260	27	6.8	.47	8.36	5.84	15.3	.59	3.53
600	48	6.1	.45	9.37	3.40	18.1	1.14	4.54
1,600	200	5.1	.36	1.12	.99	53.8	.21	27.92
250	140	4.9	.56	8.16	2.76	53.2	.19	29.71
1,650	60	5.5	.65	10.15	3.50	30.8	.32	10.74
900	90	4.9	.67	3.12	1.34	41.6	1.05	12.73
1,250	120	5.4	.47	2.18	.60	50.0	.68	16.90
750	175	5.2	.30	2.01	1.18	49.7	.49	17.06

potassium is not recovered upon extraction of soil with ammonium acetate is because it is positionally inaccessible to the replacing ammonium ions. On this basis much of the distinction between the two forms of potassium disappears. Gedroiz (19) holds that the replacement of exchangeable bases is a prolonged process and never truly complete, thus placing in the exchangeable category cations normally considered to be non-exchangeable by the relatively rapid techniques ordinarily employed in soil laboratories.

According to Kelley (33), some of the cations constituting the primary minerals are exchangeable and are gradually released by this process in the course of weathering. Ball-milling of soil colloids was found by Kelley, Dore, and Brown (34) in 1931 to render practically all of the contained potassium exchangeable. More recently Martin, Overstreet, and Hoagland (38) demonstrated the partial release of fixed rubidium to the exchangeable form as a result of prolonged grinding in a ball mill. Thus, there appears to be little if any precise theoretical distinction between exchangeable and non-exchangeable forms of potassium.

There is, nevertheless, a practical distinction. Hoagland and Martin (23) found, for example, that in most of the California soils studied by them the fraction of potassium removed by ammonium acetate was well defined. Efforts at further extraction yielded only very small quantities of potassium. This has likewise been the experience of others. In table 2 are shown the results of repeated ammonium acetate extractions of several of the soils used in the present study, the extractions being completed in about 8 days. It will be seen that leaching of the soils with ammonium acetate subsequent to the first extraction resulted in the recovery of quantities of potassium which, although appreciable, are nevertheless small in comparison with the amounts recovered in the initial extraction. It will be noted further that these quantities decrease with successive extractions. These small amounts of potassium may be looked upon either as indicating incomplete removal of "exchangeable" potassium by preceding extractions or as a solubility effect upon potassium-bearing soil minerals, or as a combination of the two.

At the time this study was begun, a number of tests were made to determine the effect of variations in the adopted procedure for the determination of exchangeable potassium. These included the use of additional ammonium acetate, longer periods of standing prior to filtration, mechanical shaking, longer periods of filtration, and heating. None of these modifications measurably increased the recovery of potassium from the soil. Even violent mechanical dispersion, effected by a 15-minute stirring of the soil-ammonium acetate mixture in a Waring Blendor, produced scarcely any effect on the amount of recoverable potassium, except in the case of one soil (No. 44-10), which was abnormally high in exchangeable potassium. The results of this treatment may be seen in table 3.

It is apparent from the foregoing discussion that the amount of potassium recovered from the soil by a single painstaking ammonium acetate extraction is a rather definite, if empirical, fraction of the total soil potassium. It is thus that we shall define the term "exchangeable potassium" for purposes of this paper.⁶ In this restricted use of the term, nothing is implied regarding the potential or ultimate exchangeability of the non-exchangeable fraction. The

⁶ This is, of course, the usual definition of exchangeable potassium.

TABLE 2. Recovery of Potassium by Repeated Extraction with Ammonium Acetate.

Soil No.	Symbol	Location	Extractions						2nd-6th incl.
			1st	2nd	3rd	4th	5th	6th	
44-3	N2	Makiki	<i>m.e./100</i> 1.34	<i>m.e./100</i> 0.030	<i>m.e./100</i> 0.022	<i>m.e./100</i> 0.0090	<i>m.e./100</i> 0.0090	<i>m.e./100</i> 0.0078	<i>m.e./100</i> 0.078
44-6	H1	Ewa	1.00	.014	.011	.0100	.0075	.0050	.048
44-10	V1	Wailuku	3.39	.028	.025	.0087	.0075	.0075	.077
44-18	N4	Puhi	.32	.0087	.013	.0062	.0050	.0050	.038
44-31	K6	Honoumu	.30	.011	.011	.0075	.0061	.0061	.042

TABLE 3. Effect of Mechanical Dispersion on Recovery of Exchangeable Potassium.

Soil No.	Symbol	Location	Without Mechani-	Mechanically	Difference
			cal Dispersion	Dispersed	
44-3	N2	Makiki	<i>m.e./100</i> 1.34	<i>m.e./100</i> 1.28	<i>m.e./100</i> -0.06
44-6	H1	Ewa	1.00	.97	-0.03
44-10	V1	Wailuku	3.39	3.54	+0.15
44-18	N4	Puhi	.32	.33	+0.01
44-24	N1	Waipahu	.47	.49	+0.02
44-31	K6	Honoumu	.30	.35	+0.05

terms "release" and "liberation," when applied to soil potassium, will refer to the conversion of non-exchangeable potassium to the exchangeable form either as detected chemically or as measured by uptake by plants.

RELEASE OF POTASSIUM UPON MOIST STORAGE

Untreated Soils

General acceptance appears to have been accorded the concept advanced by Bartholomew and Janssen (8) and Hoagland and Martin (23), and further developed by the Illinois group of workers and others that exchangeable potassium in the soil tends to exist in equilibrium with certain other forms of potassium. It has already been noted that removal of exchangeable potassium from soils followed by moist storage results in the gradual release of non-exchangeable potassium to the exchangeable form. Conversely, the addition of soluble potassium salts to certain soils not only increases the level of exchangeable potassium but causes fixation of part of the added potassium in non-exchangeable form. The latter reaction is rapid in contrast to the release of potassium. Part at least of the potassium thus fixed may be liberated upon removal of the exchangeable fraction.

In order to determine if a state of equilibrium with regard to exchangeable potassium existed in the soils collected for use in this study, the following experiment was carried out. Samples of approximately 1½ pounds of each of the 26 stock soils were placed in large Buchner funnels, wetted with distilled water, and permitted to stand for an hour. Suction was then applied until water no longer dripped from the soil, at which time the soil was transferred to a Mason jar and covered.⁷ After 12, 29, and 42 months, samples were withdrawn from the jars, air dried, and analyzed for exchangeable potassium. The results of this experiment are shown in table 4.

There appears to be little indication that the prolonged period of moist storage affected the levels of exchangeable potassium in the soils to an appreciable degree. Such changes as are in evidence are measured in hundredths, or thousandths, of a milliequivalent, and for the most part are not unidirectional. It is apparent, therefore, that the soils were either in a state approximating equilibrium with respect to exchangeable potassium, or that equilibrium following cropping is regained at an almost immeasurably slow rate. The results are in harmony with those of Bray and De Turk (12) and Wood and De Turk (58), who observed no large increases or decreases in levels of exchangeable potassium upon prolonged moist storage of untreated soils.

Soils from Which Part of Exchangeable Potassium Was Removed

In this experiment an effort was made to determine the rate at which non-exchangeable potassium is released upon moist storage as a result of the partial removal of exchangeable potassium from the soil. Such a state might be thought of as simulating a condition resulting from intensive cropping in the absence of added potassium fertilizer. Samples of 1½ pounds of each of the 26 soils

⁷ It may be noted in this connection that a study by Worsham and Sturgis (60) on the influence of increasing moisture content on the level of exchangeable soil potassium on storage showed little if any effect until saturation was reached.

TABLE 4. Effect of Moist Storage on Levels of Exchangeable Potassium in Untreated Soils.

Soil No.	Symbol	Location	Initially	After 12 mos.	After 29 mos.	After 42 mos.	Gain in 42 mos.
			<i>m.e./100</i>	<i>m.e./100</i>	<i>m.e./100</i>	<i>m.e./100</i>	<i>m.e./100</i>
44-3	N2	Makiki	1.34	1.38	1.35	1.34	0
44-6	H1	Ewa	1.00	1.02	1.03	1.03	+0.03
44-7	N3	Waialua	.49	.49	.49	.48	-.01
44-8	N3	Poamoho	.29	.28	.29	.28	-.01
44-9	N7	Waimanalo	1.34	1.40	1.43	1.40	+ .06
44-10	V1	Wailuku	3.39	3.37	3.34	3.32	-.07
44-11	V1	Puunene	1.29	1.32	1.31	1.32	+ .03
44-12	N2	Lahaina	.38	.38	.39	.38	0
44-13	N2	Paia	1.63	1.62	1.62	1.62	-.01
44-14	N2	Paia	1.00	1.03	1.03	1.00	0
44-15	T4	Kilauea	.089	.083	.085	.082	-.007
44-16	T4	Kalia	.19	.20	.22	.22	+ .03
44-17	T4	Lihue	.26	.25	.23	.23	-.03
44-18	N4	Puhi	.32	.32	.31	.31	-.01
44-19	N5	Eleele	.36	.36	.36	.35	-.01
44-20	N1	Makaweli	.26	.26	.27	.25	-.01
44-21	M	Kekaha	.51	.53	.58	.57	+ .06
44-23	N4	Aiea	.23	.23	.23	.23	0
44-24	N1	Waipahu	.47	.48	.49	.47	0
44-25	N3	Waipahu	.45	.45	.47	.44	-.01
44-26	K6	Olaa	.36	.36	.33	.33	-.03
44-27	K6	Olaa	.56	.51	.53	.51	-.05
44-28	A9	Pahala	.65	.66	.66	.64	-.01
44-29	N5	Hawi	.67	.62	.64	.65	-.02
44-30	A5	Paauiilo	.47	.45	.45	.43	-.04
44-31	K6	Honomu	.30	.35	.30	.27	-.03

were leached in large Buchner funnels with approximately 4 liters of 0.1 N hydrochloric acid. Excess acid was then eliminated by thorough washing with distilled water. The soils were air dried, thoroughly mixed, a portion taken for analysis of exchangeable potassium, and the balance wetted as previously described and stored in closed Mason jars. Four additional samples were similarly treated but with neutral 0.5 N calcium acetate, washed with distilled water, and stored. Samples were withdrawn for analysis from all treatments after 12, 31, and 41 months. The results of these tests, together with pH values resulting from the various treatments, are shown in tables 5 and 6 for the acid- and acetate-treated soils, respectively.

When table 5 is considered, it will be noted that the leaching treatment removed a large part of the exchangeable potassium from the soils, as indicated by analysis immediately following leaching. pH values were also depressed through replacement of exchangeable bases by hydrogen ions. Recovery, following displacement of exchangeable potassium, was extremely slow, the over-all increase for the 41-month period averaging only 28 pounds K_2O per acre.

It may be pointed out at this time that certain of the soils stand out from the others in regard to rates at which potassium is liberated. These soils, which are six in number (Nos. 44-3, 6, 9, 10, 11, and 21), are representative of the less weathered soils of Hawaii. In contrast to the average release of 28 pounds K_2O per acre, these six soils released amounts ranging from 38 to 113 pounds.

TABLE 5. Release of Potassium upon Moist Storage in Soils from Which Part of the Exchangeable Potassium Was Removed with 0.1 N Hydrochloric Acid.

Soil No.	Symbol	Location	pH		Exch. K in Unreated Soil	Exch. K in Treated Soils			Gain for Entire Period	
			Unreated Soil	Treated Soil		Initially	After 12 mos.	After 31 mos.		After 41 mos.
44-3	N2	Makiki	6.9	3.9	m.e./100 1.34	m.e./100 0.76	m.e./100 0.82	m.e./100 0.84	m.e./100 0.11	Lbs. K ₂ O/Acre* 104
44-6	H1	Ewa	7.0	3.6	1.00	.17	.18	.20	.04	38
44-7	N3	Waialua	6.5	4.2	.49	.13	.14	.14	.02	19
44-8	N3	Poamoho	5.4	4.3	.29	.14	.18	.18	.04	36
44-9	N7	Waimanalo	6.3	3.9	1.34	.26	.30	.30	.06	57
44-10	V1	Wailuku	6.6	3.9	3.39	.64	.71	.75	.09	85
44-11	V1	Puunene	6.5	4.2	1.29	.16	.17	.20	.04	38
44-12	N2	Lahaina	5.9	4.2	.38	.10	.10	.10	.01	9
44-13	N2	Paia	6.1	4.1	1.63	.16	.17	.17	.02	19
44-14	N2	Paia	6.1	3.9	1.00	.17	.18	.19	.02	19
44-15	T4	Kilauea	6.0	4.6	.08	.049	.051	.048	.004	4
44-16	T4	Kealia	5.8	4.4	.19	.070	.085	.093	.025	24
44-17	T4	Lihue	4.9	4.5	.26	.029	.029	.030	.007	7
44-18	N4	Puhi	5.9	4.7	.32	.049	.064	.072	.022	21
44-19	N5	Elele	6.0	4.7	.36	.079	.050	.049	.007	7
44-20	N1	Makaweli	6.3	4.5	.26	.062	.061	.064	.001	1
44-21	M	Kekaha	7.7	4.2	.51	.13	.19	.21	.12	113
44-23	N4	Aiea	6.2	4.7	.24	.040	.039	.046	.051	10
44-24	N1	Waipahu	6.8	4.6	.47	.055	.068	.073	.080	24
44-25	N3	Waipahu	6.1	4.9	.45	.057	.061	.082	.029	27
44-26	K6	Oiaa	5.1	5.0	.36017	.023	.010†	9
44-27	K6	Oiaa	4.9	5.1	.56026	.032	.042	15
44-28	A9	Pahala	5.5	5.0	.65	.046	.045	.053	.009	8
44-29	N5	Hawi	4.9	5.0	.67	.037	.037	.047	.012	11
44-30	A5	Paauilo	5.4	4.9	.47030	.034	.019†	18
44-31	K6	Honoumu	5.2	4.9	.30022	.034	.018†	17
Average									.03	28

*2,000,000 pounds oven-dry soil.
†29 months only.

TABLE 6. Release of Potassium upon Moist Storage in Soils from Which Part of the Exchangeable Potassium Was Removed with Neutral 0.5 N Calcium Acetate.

Soil No.	Symbol	Location	pH of Treated Soil	Exch. K in Untreated Soil	Exchangeable K in Treated Soils				Gain for Entire Period			
					Initially	After 12 mos.	After 31 mos.	After 41 mos.	CaAcet Leach	HCl Leach		
44-9	N7	Waimanalo	7.0	1.34	m.e./100 0.41	m.e./100 0.52	m.e./100 0.52	m.e./100 0.53	m.e./100 0.12	m.e./100 0.06	Lbs. K ₂ O/Acre 113	Lbs. K ₂ O/Acre 57
44-11	V1	Puunene	7.3	1.29	.097	.21	.21	.21	.11	.04	104	38
44-16	T4	Kealia	7.0	.19071	.088	.090	.019†	.010†	18†	9†
44-28	A9	Pahala	6.8	.65	.037	.077	.101	.101	.064	.009	60	8
Average										74	28	

*2,000,000 pounds oven-dry soil.

†29 months only.

If one turns to table 6 for the acetate-treated soils, where over-all release by the corresponding acid-treated soils is also shown, it will be seen that calcium was far more effective than hydrogen in bringing about release of potassium. The acetate-treated soils released on the average between two and three times as much potassium as those from which exchangeable potassium was removed with acid. Corresponding differential effects of calcium and hydrogen upon release of potassium on moist storage have been reported by Seatz and Winters (46) and by York and Rogers (61) for Tennessee and Alabama soils, respectively. Liming was found by Abel and Magistad (1) to increase somewhat the rate of release of potassium in potted Hawaiian pineapple soils. The previously noted more rapid release of potassium by the less weathered soils is here again in evidence in Soils 44-9 and 44-11.

Soils from Which all Exchangeable Potassium Was Removed

In an extension of the previous experiment, the effect of complete removal of exchangeable potassium upon the subsequent liberation of potassium on moist storage was determined. Exchangeable potassium was extracted with ammonium acetate from duplicate 50-gram samples of the 26 stock soils, followed by leaching with 0.5 N acetic acid and subsequent elimination of free acid with distilled water. Following removal of excess moisture in the manner previously described, the H-soils thus formed were transferred to 500-ml. Erlenmeyer flasks, stoppered, and stored. In order to investigate further the influence of calcium as the complimentary cation on the release of potassium on moist storage, five additional soils were leached, in duplicate, with neutral 0.5 N calcium acetate following extraction of exchangeable potassium. The soils were then washed with distilled water and, following determination of pH, freed of excess moisture and similarly transferred to Erlenmeyer flasks which then were stoppered and stored. At the end of 4, 12, 32, and 40 months the procedures outlined were repeated, exchangeable potassium in the ammonium acetate extracts was determined, and the soils returned to storage. Resulting data are presented in tables 7 and 8 for the H-soils and Ca-soils, respectively.

It will be seen in table 7 that a slow but continuous release of potassium occurred in the hydrogen-saturated soils throughout the period of storage. Release of potassium was most rapid during the initial stage. Quantities of potassium released ranged from 35 to nearly 400 pounds K_2O per acre for the period as a whole, with an average of 103 pounds. The less weathered soils liberated the most potassium.

Analysis of data indicates a direct relationship between release of non-exchangeable potassium by the H-soils on moist storage and levels of exchangeable potassium initially present in the soils. This relationship is significant beyond the 0.01 level ($b = 77.96$; $t = 4.90$).

Release of potassium in the Ca-soils (table 8), like that in the H-soils, was most rapid during the initial period of storage. Quantities of potassium released ranged from 114 to 517 pounds (average 271 pounds) K_2O per acre for the entire period, the greatest release being shown by the least weathered soils. Release by the Ca-soils exceeded that of corresponding H-soils by an average of 270 percent, as may be seen by the comparison values in table 8.

Comparison of rates of release of potassium with part and with all the exchangeable potassium removed prior to storage (cf. tables 5-8, inclusive) reveals a more rapid release in every case where complete removal of exchangeable

TABLE 7. Release of Potassium by H-Soils upon Moist Storage.

Soil No.	Symbol	Location	Potassium Initially Present <i>Lbs. K₂O/acre</i> †	Potassium Released* — in Lbs. K ₂ O per Acre					Total Period 40 mos.
				1st Period 4 mos.	2nd Period 8 mos.	3rd Period 20 mos.	4th Period 8 mos.	Total Period 40 mos.	
44-3	N2	Makiki	1,262	217	73	45	54	389	
44-6	H1	Ewa	942	69	23	20	18	130	
44-7	N3	Waialua	462	32	5	15	9	61	
44-8	N3	Poamoho	273	40	11	17	14	82	
44-9	N7	Waimanalo	1,262	64	15	42	15	136	
44-10	V1	Wailuku	3,193	179	47	33	28	287	
44-11	V1	Puunene	1,215	77	15	17	12	121	
44-12	N2	Lahaina	358	31	13	15	12	71	
44-13	N2	Paia	1,535	57	13	19	15	104	
44-14	N2	Paia	942	42	24	20	9	95	
44-15	T4	Kilauea	84	26	10	9	10	55	
44-16	T4	Kilauea	179	29	8	23	15	75	
44-17	T4	Lihue	245	8	13	8	6	35	
44-18	N4	Puhi	301	38	10	16	9	73	
44-19	N5	Eleele	339	22	8	11	9	50	
44-20	N1	Makaweli	245	37	8	15	10	70	
44-21	M	Kekaha	480	66	28	24	13	131	
44-23	N4	Aiea	226	18	5	14	7	44	
44-24	N1	Waipahu	443	38	7	15	8	68	
44-25	N3	Waipahu	424	38	24	19	9	90	
44-26	K6	Olaa	339	35	26	12	20	93	
44-27	K6	Olaa	528	34	23	12	6	75	
44-28	A9	Pahala	612	30	10	23	12	75	
44-29	N5	Hawi	631	41	12	11	11	75	
44-30	A5	Paauilo	442	55	5	11	11	82	
44-31	K6	Honouu	282	50	32	13	7	102	
Average				53	18	18	13	103	

*Data are averages for duplicate treatments.

†2,000,000 pounds of dry soil.

potassium was effected. More rapid release of non-exchangeable potassium with increasing displacement of exchangeable potassium appears to lend support to the equilibrium theory.

It is difficult to compare the rates of release of potassium measured in the foregoing tests with those obtained under similar conditions by others, owing to widely varying periods of storage and to the fact that release is not a linear function of the time of storage. This has been pointed out by Wood and De Turk (59) and York and Rogers (61) and already noted in connection with the results of the present study. Taking the H-soils as a basis for comparison, in Hawaiian soils release of potassium on moist storage generally appears to be less rapid than in the Illinois soils studied by Bray and De Turk (12) and Wood and De Turk (59). It is comparable, however, to that in some Iowa and Alabama soils as reported by Allaway and Pierre (2) and York and Rogers (61), respectively.

Effect of Repeated Extraction with Ammonium Acetate on Release of Potassium by H-Soils and Ca-Soils on Moist Storage

Data were presented in table 2 which showed that repeated extraction of soils with ammonium acetate subsequent to removal of exchangeable potassium resulted in the recovery of small, yet appreciable quantities of potassium. It must be assumed, therefore, that data indicating the release of potassium on moist storage (tables 7 and 8) represent, in part, potassium recovered as a result of the ammonium acetate extractions *per se* rather than to liberation attributable to storage. Comparison is made in table 9 of the quantities of potassium recovered upon four successive extractions (2 to 5, inclusive) of the soils listed in table 2 with the amounts of the element released on 40 months of moist storage of the same soils, the latter data being taken from table 7. It will be seen that from 17 to 42 percent of the potassium "released" on storage is actually attributable to repeated extraction of the soil and is independent of the time element. This should be borne in mind in any consideration of data pertaining to release of potassium on moist storage where repeated extractions are involved.

Effect of Lime on Release of Potassium in Soils from Which Potassium Was Not Displaced

The marked effect of calcium on the liberation of potassium on moist storage prompted an attempt to determine the influence of lime⁸ on acid soils from which no part of the exchangeable potassium was removed prior to storage. Six acid stock soils were treated with calcium hydroxide at rates of 0, 1, 2, and 4 tons CaO per acre (2½ million pounds of dry soil) and stored moist for a period of about 6 months. At the end of this time pH values of the soils and levels of exchangeable potassium were determined.

Results of the experiment, which are shown in table 10, reveal no evidence of release of potassium as a result of liming. It is obvious, however, that the moderate quantities of lime applied were insufficient to bring about a condition even approaching neutrality in the majority of cases. The data possibly suggest that calcium is effective in increasing the rate of liberation of potassium only when the level of exchangeable potassium has first been displaced.

⁸ Liming is not practiced in Hawaii, either on the sugar or pineapple plantations.

TABLE 8. Release of Potassium by Ca-Soils upon Moist Storage.

Soil No.	Symbol	Location	pH		Potassium Released* — in Lbs. K ₂ O per Acre†					% Increase Over H-Soils
			Untreated Soil	Treated Soil	1st Period 4 mos.	2nd Period 8 mos.	3rd Period 20 mos.	4th Period 8 mos.	Total Period 40 mos.	
44-9	N7	Waimanalo	6.3	7.0	217	198	75	27	517	380
44-11	V1	Puunene	6.5	7.3	151	122	57	24	354	293
44-16	T4	Kealia	5.8	7.0	16	41	30	27	114	152
44-24	N1	Waipahu	6.6	7.4	94	87	29	22	232	341
44-28	A9	Pahala	5.5	7.0	31	24	48	34	137	183
Average					102	94	48	27	271	270

*Data are averages for duplicate treatments.

†2,000,000 pounds oven-dry soil.

TABLE 9. Potassium Recovered by Four Successive Extractions with NH₄Ac Subsequent to Removal of Exchangeable Potassium Compared with Potassium Released upon 40 Months of Moist Storage Plus Four Extractions.

Soil No.	Symbol	K Recovered in Four Extractions (2-5, incl.)*	K Released in 40 Months of Moist Storage	K by Extraction as % of K by Moist Storage
		Lbs. K ₂ O/acre-ft.‡	Lbs. K ₂ O/acre-ft.	Lbs. K ₂ O/acre-ft.
44-3	N2	66	389	17
44-6	H1	40	130	31
44-10	V1	65	287	23
44-18	N4	31	73	42
44-31	K6	34	102	33

*Data from table 2 converted to pounds K₂O per acre-foot.

†Data from table 7.

‡2,000,000 pounds of dry soil.

TABLE 10. Effect of Lime on Release of Potassium in Soils from Which Exchangeable Potassium Was Not First Displaced* (Soils Stored Moist for 6 Months).

Soil No.	Symbol	Location	Tons Lime per Acre	pH	Exchangeable Potassium
					<i>m.e./100</i>
44-8	N3	Poamoho	0	5.1	0.32
			1	5.5	.30
			2	5.8	.31
			4	6.4	.31
44-11	V1	Puunene	0	6.3	1.25
			1	6.5	1.30
			2	6.8	1.30
			4	7.3	1.28
44-17	T4	Lihue	0	4.6	.22
			1	4.7	.24
			2	5.0	.24
			4	5.6	.23
44-27	K6	Olaa	0	4.4	.58
			1	4.5	.56
			2	4.6	.54
			4	4.7	.58
44-29	N5	Hawi	0	4.5	.68
			1	4.6	.69
			2	4.8	.61
			4	5.1	.58
44-30	A5	Paauilo	0	4.8	.48
			1	4.9	.47
			2	5.1	.47
			4	5.4	.44

*Analyses performed in part by H. H. Hagihara.

EFFECT OF DESTRUCTION OF ORGANIC MATTER ON RECOVERY OF POTASSIUM WITH AMMONIUM ACETATE

It was suggested in the course of this study that the more rapid release of potassium on moist storage in Ca-soils as compared with H-soils was possibly due to the associated increase in pH and consequent stimulation of bacterial activity resulting in an enhanced breakdown of organic matter and freeing of potassium to the action of ammonium ions. In line with this idea, Jenny and Shade (31) have suggested the possibility of an "ionic exchange impedence" caused by microorganisms or by organic colloids through formation of a protective coating over exchange positions thus retarding access of the replacing ions.

In order to examine the suggested possibility, 25-gram samples of nine of the soils employed in this study, which contained from 2.79 to 17.06 percent organic matter, were treated over a period of several hours with five 5-ml. increments of 30 percent hydrogen peroxide. At the end of this time, during which the flasks containing the soils were heated moderately, the soils were analyzed for exchangeable potassium. The results are shown in table 11, together with the original organic matter contents of the soils. Treatment with hydrogen peroxide appears to have had little if any effect upon the extractability of potassium

by ammonium acetate. It thus appears that organic matter in the soils studied neither contains appreciable quantities of potassium which are unextractable by ammonium acetate nor is capable of preventing replacement of potassium by this agent.

TABLE 11. Effect of Treatment with Hydrogen Peroxide on Recovery of Exchangeable Potassium in Soils.

Soil No.	Symbol	Location	Organic Matter	Exchangeable Potassium	
				Untreated	H ₂ O ₂
			<i>Percent</i>	<i>m.e./100</i>	<i>m.e./100</i>
44-3	N2	Makiki	2.80	1.34	1.36
44-6	H1	Ewa	2.79	1.00	1.05
44-15	T4	Kilauea	6.96	.089	.089
44-16	T4	Kalia	6.98	.19	.17
44-17	T4	Lihue	7.50	.26	.25
44-21	M	Kekaha	3.09	.51	.56
44-28	A9	Pahala	10.74	.65	.65
44-30	A5	Paauiilo	16.90	.47	.49
44-31	K6	Honomu	17.06	.30	.34

STUDIES ON CROPPED SOILS⁹

In this approach to the problem, release of potassium was determined by measuring the uptake of the element by a series of crops grown in pots and subtracting therefrom the corresponding decrease in exchangeable potassium in the soil. Twelve stock soils were potted in triplicate in Mitscherlich pots in amounts ranging from 3.0 to 5.5 kilograms, depending on the volume-weight of the soil. All pots received 9 grams P₂O₅ at the start of the experiment. Two pots of each soil were further fertilized with nitrogen at the rate of 1.1 grams per pot at the beginning of each crop, and the third with an equal quantity of nitrogen and 1.5 grams K₂O. The first three crops consisted of Sudan grass (*Sorghum Sorghum* var. *Sudanense*), but when this crop failed on one of the soils (third crop) which had not received potassium, panicum grass (*Panicum barbinode*)—a grass which thrives on soils low in exchangeable potassium—was substituted. A 14-month fallow, during which period the soils were kept moist, followed the initial crop of panicum grass. Subsequent to the fallow, three additional crops of panicum grass were grown, making a total of seven crops. The plants were grown in a greenhouse. Since tap water at the Hawaiian Sugar Planters' Association Experiment Station contains several parts per million of potassium, distilled water alone was employed throughout the study. Leachates were returned to the pots. The effect of crop growth on the level of exchangeable potassium was followed by periodic sampling and analysis of the soils. The entire experiment, including the 14-month fallow, occupied 42 months.

At harvest the plants were cut off at approximately the level of the soil and the plant material dried and weighed. Material harvested from pots of duplicate treatments was weighed and analyzed separately. Plant material from complete treatments was not analyzed for potassium, except in the case of the fifth crop. Crops 1 and 2 were combined for purposes of analysis.

⁹ This phase of the study was carried out in cooperation with the Agronomy Department, Experiment Station, Hawaiian Sugar Planters' Association.

Effect of Cropping without Added Potassium on Levels of Exchangeable Potassium in Soils

Consideration may first be given to the effect which cropping produced on levels of exchangeable soil potassium. Exchangeable potassium data for the soils are contained in table 12, together with initial and final pH and potassium saturation values. Percentage reductions in levels of exchangeable potassium caused by cropping are also indicated. For purposes of illustration some of the results are reproduced graphically in figure 1.

Decreases in exchangeable potassium were extremely rapid in all soils which were well supplied with exchangeable potassium initially. It is probable that decreases were more rapid than indicated since the soils were not sampled until the end of the second crop, 5½ months after the test was begun. By the end of the third crop, at 10 months, levels had been reached which were lowered but little by succeeding crops. Final values in all soils but two were less than 0.10 milliequivalent per 100 grams of soil. The slight rise in level of exchangeable potassium in Soil 44-3 at the second sampling of the soil (10 months) is associated with the complete failure of the immediately preceding crop. Hence, the increase may have resulted from decomposition of plant roots, coupled with the absence of a growing crop to absorb the freed potassium. The inability of the plants to lower further the levels of exchangeable potassium (one of the soils contained 0.10 and another 0.20 milliequivalent at the final harvest), even though

TABLE 12. Effect of Cropping without Added Potassium on Levels of Exchangeable Potassium.

Soil No.	Symbol	Location	pH Values		K Saturation	
			Initial	Final	Initial	Final
44-3	N2	Makiki	6.9	6.5	<i>Percent</i> 3.74	<i>Percent</i> 0.56
44-6	H1	Ewa	7.0	6.1	3.91	.36
44-8	N3	Poamoho	5.4	4.7	2.00	.59
44-12	V1	Lahaina	5.9	5.2	2.47	.38
44-14	N2	Paia	6.1	5.3	5.75	.57
44-15	T4	Kilauea	6.0	5.2	.49	.29
44-18	N4	Puhi	5.9	5.3	1.74	.44
44-20	N1	Makaweli	6.3	5.3	1.76	.51
44-25	N3	Waipahu	6.1	5.3	2.49	.46
44-26	K6	Olaa	5.1	4.7	.67	.069
44-29	N5	Hawi	4.9	4.6	1.61	.13
44-30	A5	Paauiilo	5.4	4.6	.94	.068
Average						

*Data are averages for duplicate pots.

lack of this nutrient was causing restricted growth as early as the first crop, indicates that varying proportions of the exchangeable potassium were not available to the crops. Reference to table 12 indicates that on the average values for exchangeable potassium at the conclusion of the experiment were 20 percent of initial values. Similar results have been obtained on other soils and for other crops by Hoagland and Martin (23), Chandler, Peech, and Chang (14), Stewart and Volk (74), and by Bear, Prince, and Malcolm (9). This unavailability of potassium to plants at these low levels is probably explainable in part by the work of Jenny and Ayers (27) and of Tyner (48), who found that the availability of exchangeable potassium to plants decreased with decreasing degree of potassium saturation of the soil. This is not the complete answer, however, in the present study. Although the degree of potassium saturation was not reduced much below 0.60 percent in a number of the soils, it was lowered to less than 0.10 percent in others.

Exchangeable potassium increased in all but one of the soils during the 14-month fallow between the fourth and fifth crops. Increases were very small, however, and were probably due in part to liberation of potassium from decomposing roots. The results do not appear to harmonize with those of Volk (51) and of De Turk, as reported by De Turk, Wood, and Bray (16), who observed rather rapid recoveries of levels of exchangeable potassium upon fallow following displacement of exchangeable potassium as a result of cropping. The small increases associated with the fallow are of the same order as those resulting from moist storage in the present study.

Bartholomew (7), Murphy (41), and Walker, as reported by Worsham and Sturgis (60), have reported release of non-exchangeable potassium in soils resulting from decomposition of organic matter. It might be anticipated, therefore, that decomposition of the mass of roots accruing from previous crops would result in appreciable release of non-exchangeable potassium with resulting increases in levels of exchangeable potassium during the fallow period. As already noted, however, increases were very small. Allowance must also be made for potassium contained in the roots as well as for release of potassium which is independent of the presence of organic matter. Hoagland and Martin (23) are disinclined to assign to organic matter any influence on the level of exchangeable potassium other than that resulting from liberation of potassium contained in the organic matter itself.

Crop Yields

Yield data for the seven crops are shown in table 13. Much of the irregularity in yields is the result of different crops, of different lengths of crops, of ratoon as well as plant crops, and of abnormal soil conditions caused by repeated cropping in small pots. Yields of Sudan grass diminished markedly in all pots which received no potassium fertilizer, resulting in complete failure in the third crop in the case of soil No. 44-3. Moderate declines in yields occurred in the completely fertilized pots also. Yields improved with the substitution of panicum for Sudan grass in the fourth crop. Dry weights in the sixth crop dropped off following the preceding plant crop but increased again upon replanting in the seventh and final crop. Although a number of the soils originally were abundantly supplied with exchangeable potassium, as judged by usual standards, only one

TABLE 13. Crop Yields.*

Soil No.	Symbol	Location	Treatment	Dry Weights of Grass in Grams Per Pot†														
				Crop 1		Crop 2		Crop 3		Crop 4		Crop 5		Crop 6		Crop 7		
				Plant	Ratoon	Plant	Ratoon	Plant	Ratoon	Plant	Ratoon	Plant	Ratoon	Plant	Ratoon	Plant	Ratoon	Plant
44-3	N2	Makiki	N,P N,P,K	159 180	90 171	3 169	41 251	164 188	90 300	153 341								
44-6	H1	Ewa	N,P, N,P,K	143 168	123 163	72 155	71 299	154 206	48 284	132 382								
44-8	N3	Poamoho	N,P N,P,K	142 162	90 156	55 132	139 253	111 194	41 189	105 326								
44-12	N2	Lahaina	N,P N,P,K	167 198	66 159	21 154	81 252	137 195	37 280	117 353								
44-14	N2	Paia	N,P N,P,K	180 176	135 160	13 151	81 266	161 195	47 259	128 329								
44-15	T4	Kilauea	N,P N,P,K	103 153	41 146	16 90	93 277	88 185	21 285	88 372								
44-18	N4	Puhi	N,P N,P,K	150 195	75 179	52 141	91 290	108 213	40 292	99 370								
44-20	N1	Makaweli	N,P N,P,K	141 201	77 157	40 134	85 276	115 194	44 278	104 368								
44-25	N3	Waipahu	N,P N,P,K	169 194	89 157	19 135	67 243	116 167	58 251	112 333								
44-26	K6	Olaa	N,P N,P,K	70 137	62 143	36 93	79 253	85 204	21 246	95 373								
44-29	N5	Hawi	N,P N,P,K	139 149	80 144	30 69	117 270	88 184	32 198	111 312								
44-30	A5	Paauiilo	N,P N,P,K	107 139	100 152	30 74	93 263	90 171	22 211	102 306								

*Crops 1-3, Sudan grass; 4-7, panicum grass.

†Data for N,P treatments represent average values for duplicate pots.

(No. 44-14) produced yields, in the absence of added potassium, comparable with those on the completely fertilized soil. This only occurred in the first crop. Yields are in keeping with the rapid depletion of exchangeable potassium as evidenced in figure 1 and table 12. In soils receiving no potassium fertilizer practically all growth after the third crop was made at the expense of non-exchangeable potassium. Although in the final harvest, yields, in the absence of applied potassium, averaged only about one-third those on the corresponding completely fertilized soils, there is no reason to believe that growth would not have continued on soils receiving nitrogen and phosphorus only had the study been continued. Photographs of some of the plants in the third, fifth, and sixth crops are shown in plates 1, 2, and 3.

Levels of Potassium in Plants

Percentages of potassium in the aerial portions of the crops grown without added potassium are shown in table 14. Levels of potassium in the completely fertilized plants are also indicated in the case of the fifth crop. Potassium levels in Sudan grass dropped sharply from crops 1 and 2 (combined) to the third crop. A less marked and irregular downward trend is seen also in the four suc-

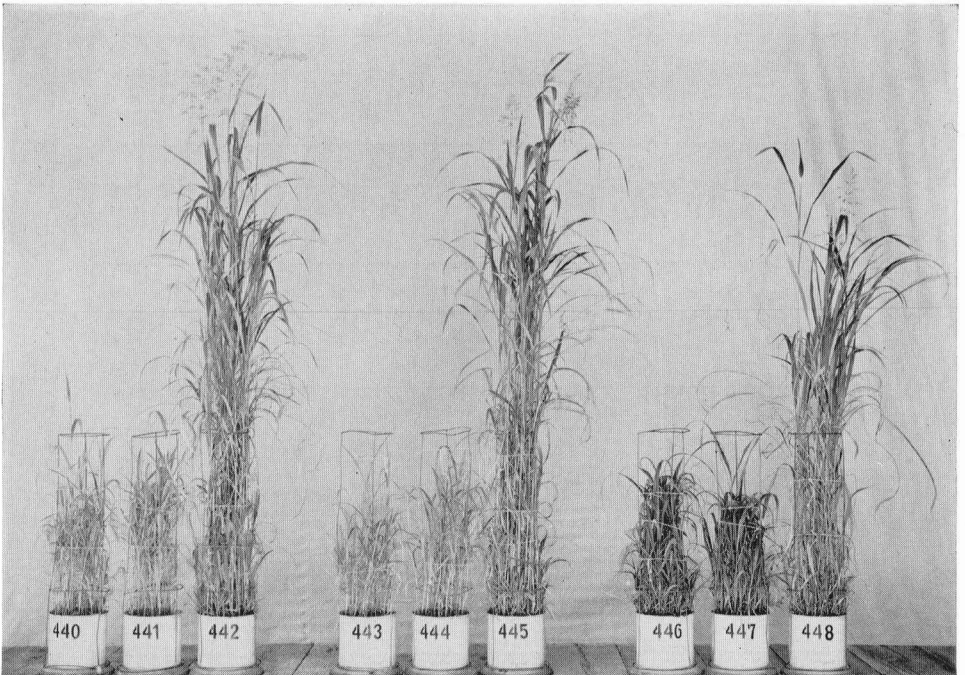


Plate 1. Photograph illustrates growth of Sudan grass in third crop. The two pots on the left in each case received N and P only; the pot on the right N, P, and K (pots 440-442, soil No. 44-12; pots 443-445, soil No. 44-14; pots 446-448, soil No. 44-15).

TABLE 14. Levels of Potassium in Plants.*

Soil No.	Symbol	Location	Treatment	Potassium (K) in Percent of Dry Matter†					
				Crops 1 & 2	Crop 3	Crop 4	Crop 5	Crop 6	Crop 7
44-3	N2	Makiki	N,P N,P,K	1.20	0.95	1.41	0.23 .97	0.30	0.34
44-6	H1	Ewa	N,P N,P,K	.85	.40	.33	.14 .78	.13	.15
44-8	N3	Poamoho	N,P N,P,K	.37	.15	.106	.21 .87	.13	.105
44-12	N2	Lahaina	N,P N,P,K,	.45	.31	.25	.15 .84	.16	.105
44-14	N2	Paia	N,P N,P,K	.89	.49	.38	.15 .98	.16	.101
44-15	T4	Kilauea	N,P N,P,K	.27	.17	.081	.16 .88	.14	.080
44-18	N4	Puhi	N,P N,P,K	.35	.15	.13	.19 .85	.12	.089
44-20	N1	Makaweli	N,P N,P,K	.36	.30	.16	.17 .94	.12	.107
44-25	N3	Waipahu	N,P N,P,K	.45	.31	.27	.20 .96	.13	.13
44-26	K6	Olaa	N,P N,P,K	.57	.18	.089	.18 .93	.15	.099
44-29	N5	Hawi	N,P N,P,K	.46	.20	.12	.20 1.03	.13	.093
44-30	A5	Paauilo	N,P N,P,K	.55	.21	.088	.17 .85	.14	.096

*Crops 1-3, Sudan grass; Crops 4-7, panicum grass.

†Results for N,P treatments are averages of duplicate pots.

ceeding crops of panicum grass. Similar reduction in potassium content of plants upon continuous cropping without added potassium has previously been reported (14, 61). Data for the complete series (crop 5) show these plants in every case to possess much higher levels of potassium than those not receiving potassium fertilizer.

Although somewhat outside the scope of this paper, it is of interest to consider the relationship which exists between levels of potassium in the first two crops of Sudan grass (combined) and supplies of exchangeable potassium initially present. It is of importance from the standpoint of assessing the supplies of soil potassium available to plants by chemical analysis of the soil. The relationship, illustrated in figure 2, is significant beyond the 0.01 level ($b = 0.71$; $t = 10.8$) despite the fact that part of the potassium in the plants was derived from non-exchangeable sources. Remaining supplies of exchangeable potassium had become fairly well equalized by the end of the second crop, except in the case of Soil 44-3. This soil, which possessed higher levels of exchangeable potassium at all times than the other soils, consistently produced crops which were correspondingly higher in potassium.

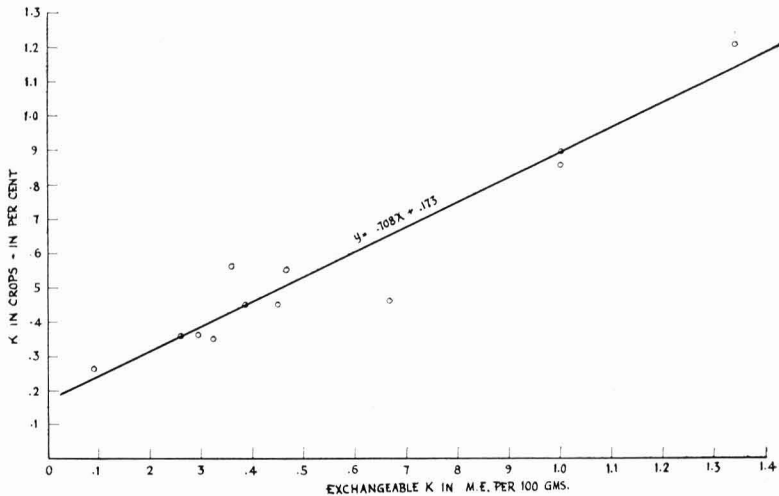


Figure 2—Relationship between percentages of potassium in crops 1 and 2 (combined) and initial levels of exchangeable potassium in soils.

Release of Non-exchangeable Potassium as a Result of Cropping

The quantities of potassium liberated coincident with cropping, together with the total amounts of the element taken up by the crops, and derived data are shown in table 15. Release was most rapid in the early stages of the experiment, as was the case upon moist storage. The first two crops together accounted, on the average, for nearly half the total quantity of potassium liberated. Total release for the seven crops (42 months) ranged from 325 to 1,256 pounds K_2O per acre, with an average of 699 pounds. Actually, release was more rapid than the data indicate. The 42-month period included a 14-month fallow during which liberation of potassium proceeded at a far slower rate than when the soils were cropped. Soils 44-26 and 44-30 are ash-derived soils of low volume-weight. Since the data are expressed in terms of pounds K_2O per 2 million pounds of soil, values for these two soils correspond to proportionately greater volumes of soil.

The foregoing results may be compared with those of Bear, Prince, and Malcolm in New Jersey (9), who observed release of potassium in potted soils ranging from practically nothing to 235 pounds K_2O per acre in 1 year. They may also be compared with results of Chandler, Peech, and Chang (14) in New York, who reported release of from 41 to 203 pounds K per acre in 261 days, and with those of Stewart and Volk (47), who found that certain Wisconsin soils liberated an average of 88 pounds K_2O per acre in 4 years. Similar results have been reported by other mainland workers. In Hawaii, Magistad (1) grew successive crops of sorghum in potted pineapple soils and observed average annual releases of about 75 and 100 pounds K_2O per acre on unlimed and limed soils, respectively.

Comparison of data in tables 12 and 15 indicates that the plants were able to derive large quantities of potassium from non-exchangeable sources in the presence of the exchangeable form. This was most pronounced during the first two crops when levels of exchangeable potassium were highest and release of potassium was most rapid.

The more rapid release of potassium by the less weathered soils is not so much in evidence where release was induced by cropping. Thus, although one of the two less weathered soils (No. 44-3) released the most potassium, the other (No. 44-6) liberated less than a number of the more weathered soils (table 12).

Reference to figure 3 shows a close relationship, which analysis of data indicates is highly significant ($b = 14.0$; $t = 8.9$), between release by cropping and upon moist storage for the 10 more highly weathered soils. The two less weathered soils (44-3 and 6), however, appear to be in a separate category entirely. As a matter of fact, the relationship is still significant if Soil 44-3 is

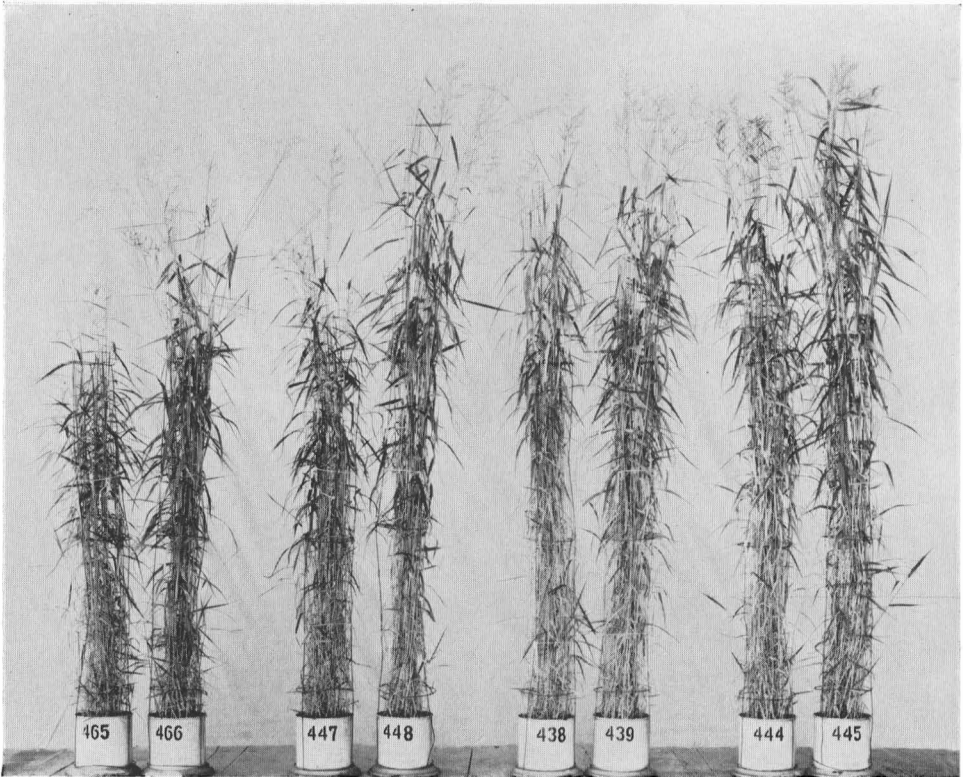


Plate 2. Panicum grass in fifth crop (first crop following fallow). Differentiation was less marked in this crop. Pot on left in each pair received N and P only; pot on right complete fertilizer (pots 165-166, soil No. 44-30; pots 447-448, soil No. 44-15; pots 438-439, soil No. 44-8; pots 444-445, soil No. 44-14).

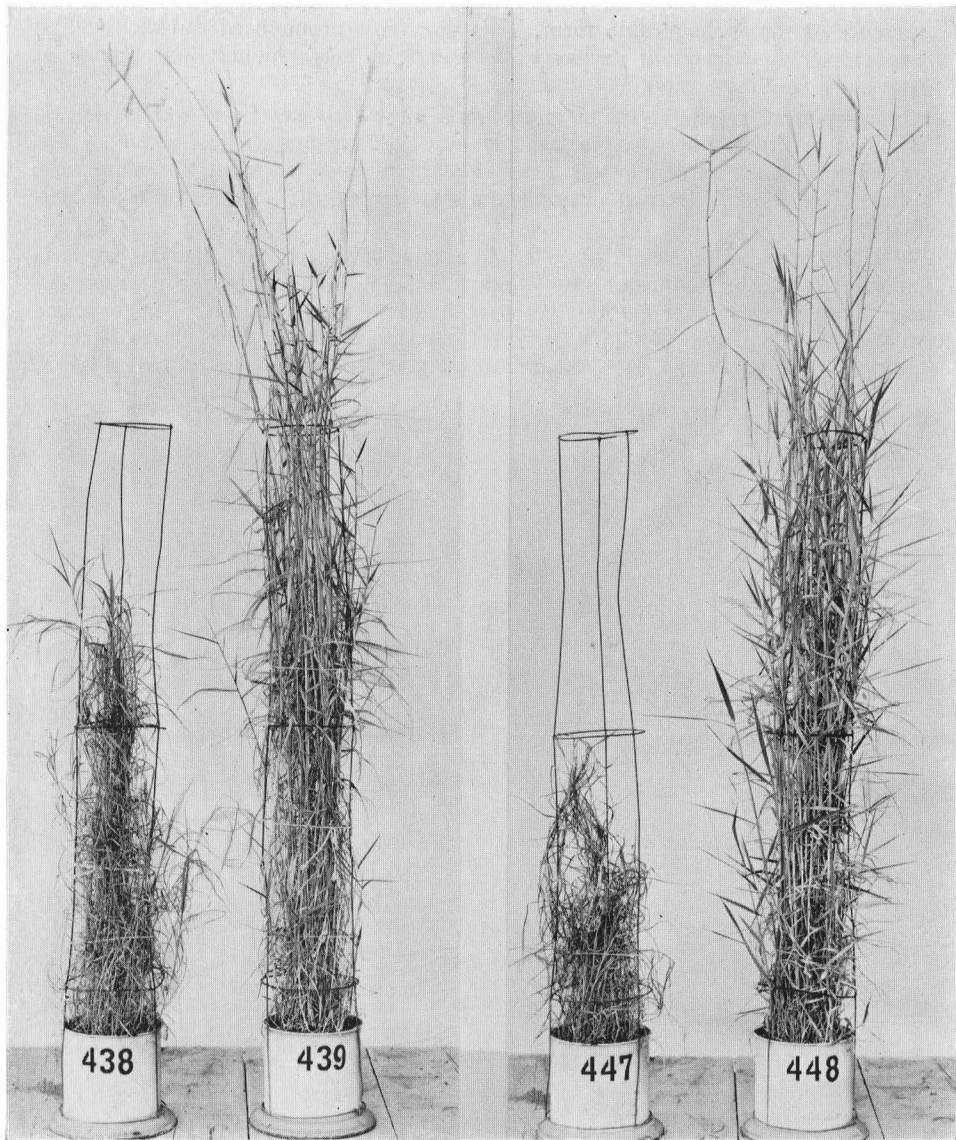


Plate 3. Left: Growth of panicum grass with and without added potassium in sixth crop. Soil No. 44-8. Pot 438 received N and P only; pot 439 complete fertilizer.

Right: Illustration of differential growth of panicum grass in sixth crop. Soil No. 44-15. Pot 447 was fertilized with N and P only; pot 448 received N, P, and K.

TABLE 15. Release of Non-exchangeable Potassium upon Cropping* (total period 42 months, including 14 months of fallow; all data are average for duplicate pots).

Soil No.	Symbol	Location	Total K Taken Up Lbs. K ₂ O/Ar	Non-Exchangeable K Released in							Non-Exch. K as % of Total Taken Up	Total K Taken Up as % of Total Soil K	Non-Exch. K Taken Up as % of Total Soil K
				Crops 1 & 2	Crop 3	Crop 4	Crop 5	Crop 6	Crop 7	Total			
44-3	N2	Makiki	2,351	509	49	154	194	138	212	1,256	53.4	23.0	12.3
44-6	H1	Ewa	1,539	254	127	103	100	31	76	691	44.9	19.2	8.6
44-8	N3	Poamoho	884	330	45	74	142	33	55	679	76.8	2.9	2.3
44-12	N2	Lahaina	884	264	35	82	113	32	59	585	66.2	9.4	6.2
44-14	N2	Paia	1,697	490	30	109	120	35	50	834	49.1	8.7	4.3
44-15	T4	Kilauea	363	141	16	42	73	15	38	325	89.5	2.5	2.3
44-18	N4	Puhi	781	245	30	57	126	29	57	544	69.7	3.4	2.4
44-20	N1	Makaweli	807	292	31	73	118	32	71	617	76.5	5.6	4.3
44-25	N3	Waipahu	1,106	367	39	78	143	46	71	744	67.3	4.9	3.3
44-26	K6	Olaa	1,185	490	63	67	160	33	77	890	75.1	28.2	21.2
44-29	N5	Hawi	1,112	195	44	54	137	32	60	522	46.9	5.3	2.5
44-30	A5	Paaulo	1,129	377	32	63	140	27	57	701	62.1	8.2	5.2
Average			1,166	330	45	80	131	40	74	699	64.8	10.1	6.2

*Crops 1-3, Sudan grass; Crops 4-7, panicum grass.

†2,000,000 pounds dry soil.

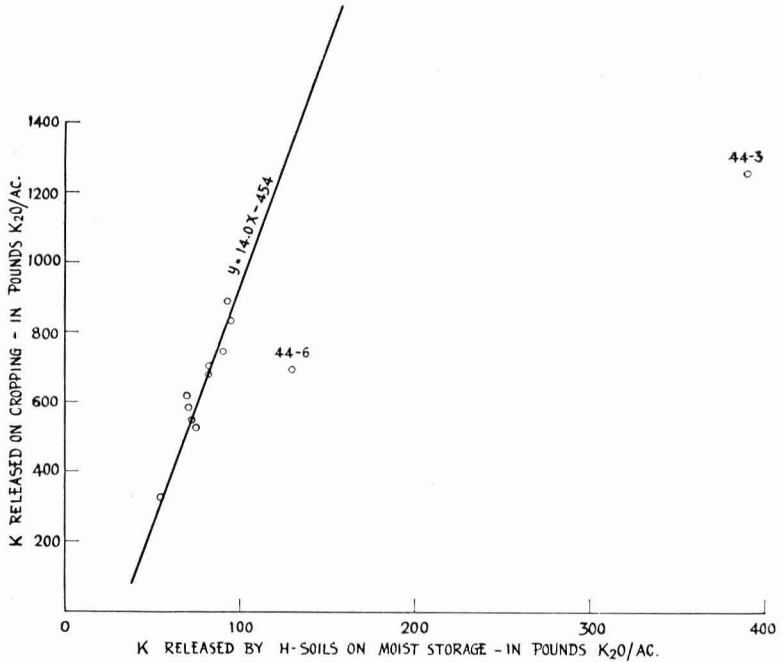


Figure 3—Relationship between non-exchangeable potassium released on cropping and on moist storage of H-soils.

included with the more weathered soils, but the significance is lost if inclusion is extended to Soil 44-6. Had a larger number of the less weathered soils been cropped, it is quite possible that a corresponding, but different, relationship would also have been found for these soils.

A direct relationship, significant beyond the 0.01 level ($b = 1.26$; $t = 3.39$), was found between release of potassium on cropping and initial levels of exchangeable potassium. The number of comparisons is small, however.

The significance of non-exchangeable potassium as a source of this nutrient for growing plants is illustrated in the third from the last column in table 15. From about 45 to nearly 90 percent, or an average of about 65 percent, of the potassium absorbed by the seven crops was derived from sources which were non-exchangeable at the beginning of the experiment. These results are comparable to those reported by Stewart and Volk (47) in 1946 in a similar 4-year study of Alabama soils.

The drain which intensive cropping under pot conditions in the absence of applied potassium is able to exert upon the supply of total soil potassium may be seen by reference to the second from the last column in table 15. Quantities of potassium taken up by the seven crops range from 2.5 to as much as 28.2 percent of the entire amounts of soil potassium initially present, averaging about 10 percent for the soils as a whole. Non-exchangeable potassium alone taken up by the crops comprised from 2.3 to 21.2 percent (average 6.2) of the total soil potassium present at the beginning of the experiment.

RELEASE OF NON-EXCHANGEABLE POTASSIUM UPON ELECTRODIALYSIS

Following the early developmental studies of Bradfield and Mattson on electro dialysis, a number of attempts were made to relate the quantity of potassium recovered from soils by this process to the exchangeable potassium. The general conclusion resulting from studies of Mattson (39), McGeorge (40), Wilson (56), Salgado (45), and others has been that they are essentially one and the same in quantity. Electro dialysis accomplishes by hydrolysis what the exchanging cation in extraction of the soil with a salt solution accomplishes by direct replacement. In these studies, however, electro dialysis was generally operative for a rather short period, often ending when neutrality in the catholyte was approximated.

It has been the experience of the writer in electro dialysing Hawaiian soils that, although they yield within a period of 24 hours an amount of potassium equivalent to the exchangeable fraction, further electro dialysis results in the recovery of still more potassium. The additional amount may be almost negligible or it may be very large. Gilligan (20) has similarly reported electro dialysable potassium in excess of the exchangeable form on Delaware soils. In this connection Oden and Wijkstrom, as reported by Loddesol (35), warn of the necessity for distinguishing in electro dialysis between the exchangeable cations and cations liberated by "weathering."

It seemed worth while to determine if potassium in excess of the exchangeable equivalent recovered upon electro dialysis could be related quantitatively to potassium released in more conventional ways. Should such a relationship be established it could result in a simple and comparatively rapid means of appraising the relative ability of a soil to supply crops with potassium from non-exchangeable sources. To this end a number of soils were electro dialysed for periods ranging from 15 to 30 days. A Mattson type cell, with power pack delivering approximately 100 volts, and cellophane membranes were used. The results secured on four of the soils, so selected as to indicate the range of the

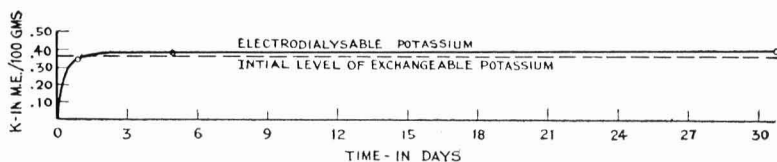


Figure 4—Electro dialysable potassium in relation to exchangeable potassium in a Hydrol Humic Latosol (K6), soil No. 44-26.

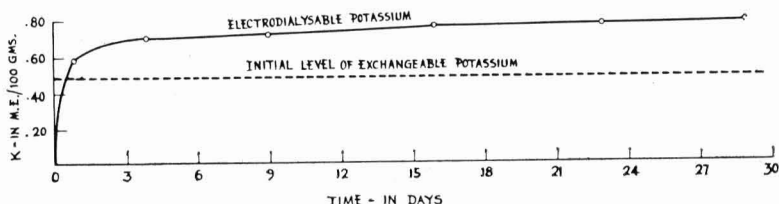


Figure 5—Electro dialysable potassium in relation to exchangeable potassium in a Low Humic Latosol (N3), soil No. 44-7.

data obtained, are presented graphically in figures 4 to 7, inclusive. In each of these charts a dotted line has been projected horizontally from the point on the Y-axis corresponding to the level of exchangeable potassium initially present in the soil. The vertical distance between this line and the curve above it represents the cumulative release of non-exchangeable potassium for a given period.

These figures indicate very rapid initial recovery of potassium. Amounts equal to the exchangeable fraction were extracted from the soil in the course of the first day. Subsequent to this period, rates of recovery decreased markedly in all cases. Soil 44-26 (fig. 4) is typical of a number of soils that yielded, upon electro dialysis, amounts of potassium which were but slightly in excess of the

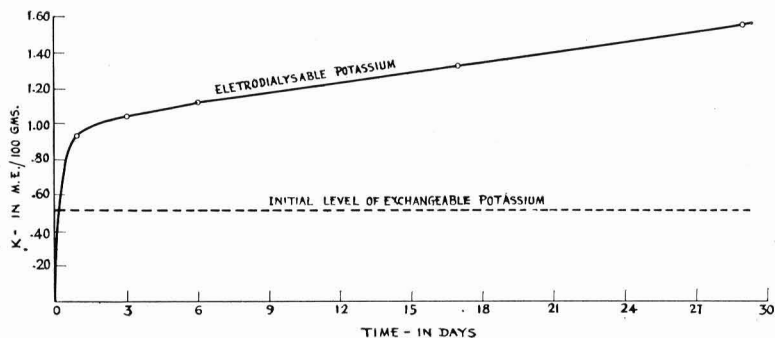


Figure 6—Electrodialysable potassium in relation to exchangeable potassium in an Intrazonal Dark Magnesium Clay (M), soil No. 44-21.

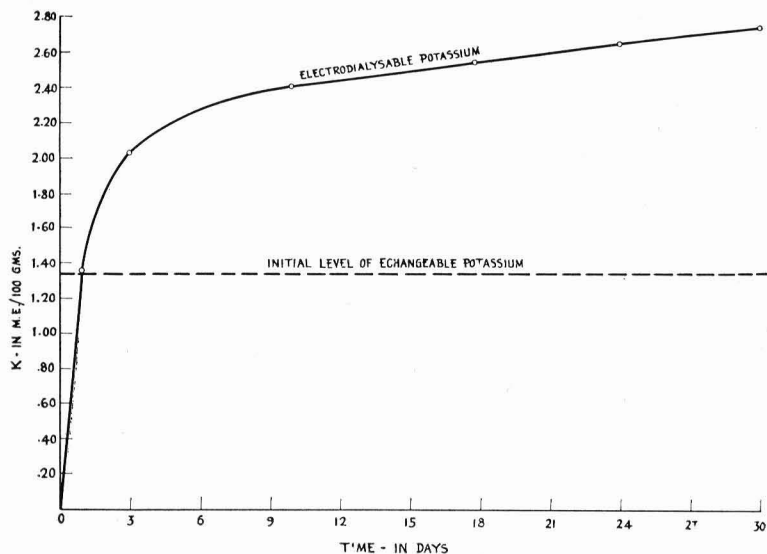


Figure 7—Relation between electrodeionisable and exchangeable potassium in a Low Humic Latosol (N2), soil No. 44-3.

exchangeable fraction. Figures 5, 6, and 7 indicate the recovery of very substantial quantities of non-exchangeable potassium. In one case electrolysable potassium was equal to twice the exchangeable fraction. Shapes of the curves for most of the soils electrolysed suggest that continued electrolysis would result in the recovery of still further quantities of potassium.

In a closely related study, exchangeable potassium was removed from a number of soils with ammonium acetate, following which the soils were washed with 0.05 N hydrochloric acid and subjected to electrolysis for periods ranging from 15 to 30 days. Some of the results are pictured graphically in figure 8. Even with the exchangeable potassium first removed, recovery of potassium did not proceed at uniform rates, but was most rapid during the initial periods. Further evidence that non-exchangeable potassium is differentially released upon electrolysis will be seen upon reference to table 16. The less weathered soils generally released the most potassium upon electrolysis.

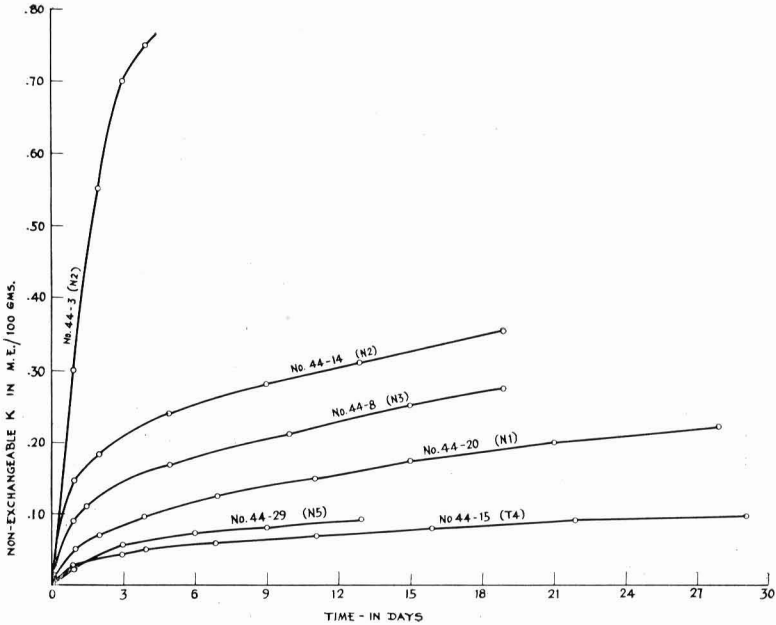


Figure 8—Curves show cumulative release of non-exchangeable potassium upon electrolysis.

Comparison of rates of release of non-exchangeable potassium by electrolysis and on moist storage of H-soils is made in figure 9. Data for electrolysable potassium are based upon recovery during the initial 15-day period. The relationship indicated with these 12 soils is significant statistically ($b = .24$; $t = 5.4$). The number of comparisons is small, however, and elimination of the two highest values would void the significance of the relationship. The number of soils which were both cropped and electrolysed was too small to permit a satisfactory corresponding analysis of data. Further work would be required to determine if this simple and comparatively rapid technique could be used for estimating rates of release of non-exchangeable potassium in Hawaiian soils.

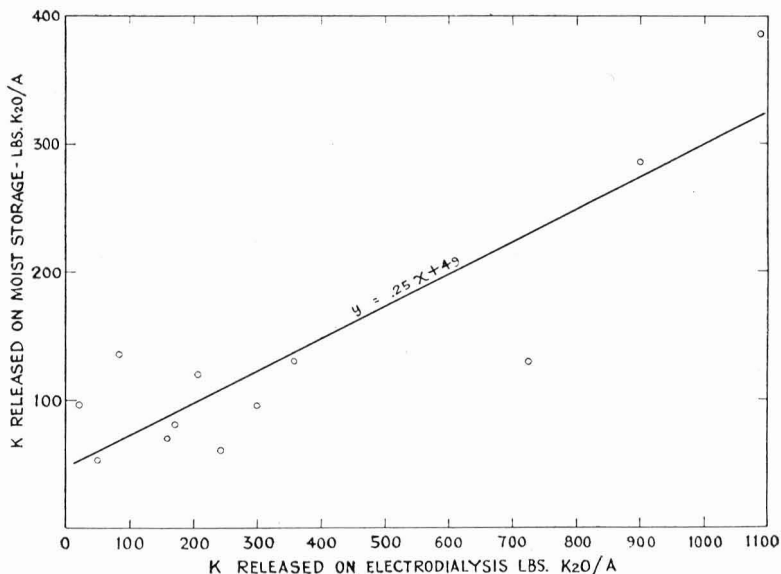


Figure 9—Relation between non-exchangeable potassium released on moist storage and by electrodiagnosis.

TABLE 16. Release of Non-exchangeable Potassium upon Electrodiagnosis.

Soil No.	Symbol	Location	Potassium Released—in Lbs. K ₂ O/Acre*		
			1st 15 Days	2nd 15 Days	Total 30 Days
44-3	N2	Makiki	1,092	217	1,309
44-6	H1	Ewa	357	48	405
44-7	N3	Waialua	245	19	264
44-8	N3	Poamoho	170	47	217
44-9	N7	Waimanalo	85	75	160
44-10	V1	Wailuku	904	113	1,017
44-11	V1	Puunene	207	57	264
44-14	N2	Paia	301	---	---
44-15	T4	Kilauea	64	30	94
44-20	N1	Makaweli	160	52	212
44-21	M	Kekaha	725	274	999
44-26	K6	Olaa	19	9	28

*2,000,000 pounds oven-dry soil.

SOLUBILITY OF NON-EXCHANGEABLE POTASSIUM IN HYDROCHLORIC ACID

Potassium extracted by Fraps (18) with 12 percent hydrochloric acid from Texas soils was found to be correlated with the quantities of the nutrient absorbed by potted plants. Wood and De Turk (58) in 1940 showed that the abilities of certain Illinois soils to maintain levels of exchangeable potassium under continued cropping were related to the potassium extractable by boiling with N nitric acid less the exchangeable fraction. Attoe and Truog (4) in 1945 recognized a "moderately available" category consisting of potassium

soluble in 0.5 *N* hydrochloric acid. More recently Joffe and Levine (32) found that fixed potassium, although resisting the action of hot 0.1 *N* hydrochloric acid, could be dissolved in its entirety by hot *N* hydrochloric acid. Primarily because of its solubility effect upon the potassium mineral biotite, van der Marel (49) recently recommended 25 percent hydrochloric acid for the determination of "available" potassium in *tropical* soils. If some such simple empirical technique were found to give results on Hawaiian soils which could be correlated with the release of non-exchangeable potassium to growing crops, it might well prove a welcome substitute for the laborious and time-consuming biological and moist storage procedures.

As a first step in this direction a preliminary test was conducted in order to ascertain the strength of acid necessary to extract quantities of potassium from soils approximating those released on cropping. Twenty-five-gram samples of four soils were treated with 100-ml. portions of 0.5 *N*, *N*, 2 *N*, 3 *N*, and 4 *N* hydrochloric acid. The flasks containing the soils were then placed on an electric hot plate, covered with watch glasses to retard loss by evaporation, and brought quickly to a temperature of 95°C. After 1 hour at this temperature, during which time the flasks were shaken occasionally, the soils were filtered and potassium in the extracts determined. The quantities of potassium extracted from the soils in this manner, minus the exchangeable fraction, are shown in table 17. For the purpose of comparison, the quantities of potassium released on cropping are also indicated.

TABLE 17. Non-exchangeable Potassium Soluble in Various Strengths of Hydrochloric Acid.

Soil No.	Symbol	Location	Non-Exch. K Released on Cropping	Solubility of K—in Lbs. K ₂ O/Acre*				
				0.5 <i>N</i>	<i>N</i>	2 <i>N</i>	3 <i>N</i>	4 <i>N</i>
			<i>Lbs. K₂O/Acre*</i>					
44-3	N2	Makiki	1,256	445	1,045	1,395	2,150	3,670
44-12	N2	Lahaina	585	415	415	585	715	1,100
44-15	T4	Kilauea	325	255	255	358	400	425
44-30	A5	Paauiilo	701	50	-----	105	190	460

*2,000,000 pounds oven-dry soil.

Recovery of non-exchangeable potassium increased with increasing strength of acid, extraction at the higher concentrations being generally proportionately higher. Concentrations of hydrochloric acid between one and two normal are seen to have effected the solution of amounts of potassium, of the order desired, in the case of the first three soils listed in the table. For the fourth, a Humic Latosol, a higher concentration is indicated. As a result of a number of considerations, not excluding the fact that at concentrations of two normal and above copious quantities of sesquioxides were extracted from all of the soils, an acid strength of one normal was selected. Determination of non-exchangeable potassium soluble in *N* hydrochloric acid in the 26 stock soils was carried out as outlined above except that exchangeable potassium was first removed with ammonium acetate and the soils washed with 0.05 *N* hydrochloric acid. The data obtained are presented in table 18.

Hot normal hydrochloric acid extracted from the soils quantities of non-exchangeable potassium ranging from 75 to 1,338 pounds K₂O per acre. As would be expected from the preliminary results, amounts of potassium extracted

TABLE 18. Non-Exchangeable Potassium Extracted by Hot N Hydrochloric Acid.

Soil No.	Symbol	Location	Potassium <i>Lbs. K₂O/Acre*</i>	Soil No.	Symbol	Location	Potassium <i>Lbs. K₂O/Acre*</i>
44-3	N2	Makiki	1,338	44-18	N4	Puhi	355
44-6	H1	Ewa	290	44-19	N5	Eleele	234
44-7	N3	Waialua	430	44-20	N1	Makaweli	332
44-8	N3	Poamoho	559	44-21	M	Kekaha	999
44-9	N7	Waimanalo	339	44-23	N4	Aiea	196
44-10	V1	Wailuku	768	44-24	N1	Waipahu	353
44-11	V1	Puunene	479	44-25	N3	Waipahu	382
44-12	N2	Lahaina	359	44-26	K6	Olaa	81
44-13	N2	Paia	425	44-27	K6	Olaa	82
44-14	N2	Paia	463	44-28	A9	Pahala	268
44-15	T4	Kilauea	214	44-29	N5	Hawi	92
44-16	T4	Kealia	315	44-30	A5	Paaulo	87
44-17	T4	Lihue	336	44-31	K6	Honoumu	75

*2,000,000 pounds oven-dry soil.

from the Humic Latosol of the island of Hawaii (No. 44-30) and the closely related Hydrol Humic Latosols (Nos. 44-26, 27, 31) were relatively very low. A comparable figure was also obtained for still another soil of this island, No. 44-29, a Low Humic Latosol.

Comparison of acid-extractable non-exchangeable potassium with that released upon moist storage by the H-soils and upon cropping shows direct relationships which are significant beyond the 0.01 and 0.05¹⁰ levels, respectively. The relationships suggest a short cut to the estimation of the power of Hawaiian soils to liberate non-exchangeable potassium. Differentiation between soils differing widely in this respect should prove a simple matter. Further study, possibly involving extraction with other acids, would be necessary, however, to determine whether the method is suited to distinguishing between soils which differ but moderately in releasing power. It is evident that the Hydrol Humic Latosols and certain associated soils would require separate treatment.

EFFECT OF AIR DRYING AND OF HEATING ON RELEASE OF POTASSIUM

Occasionally samples of field soils brought into the laboratory have been analyzed for exchangeable potassium prior to air drying. The results, when expressed on the oven-dry basis, have not differed very much from those obtained by analysis of the air-dry soils when similarly expressed. Attoe (3) in 1946 showed that air drying Wisconsin soils at room temperature resulted in release of non-exchangeable potassium amounting to from about 4 to 90 percent of the exchangeable fraction present in the moist soil. He further demonstrated that the release increased with decreasing relative humidity. Bray and De Turk (12) heated soils for 6 days at 200°C. and found that some of the soils released potassium while it was fixed by others. The soils studied by the latter workers included two Hawaiian soils. One, a "coral soil," fixed 108 pounds of K₂O per acre; the other, a "high lime soil," released 7 pounds per acre.

Consideration was given to this phase of the liberation of non-exchangeable potassium in soils in the following manner. Samples of 10 soils representing as many soil families and comprising six soil groups were collected from sugar cane and pineapple fields, as well as from virgin areas. The specimens were placed almost at once in closed Mason jars. The top few inches of soil were discarded in taking the samples, where it seemed advisable, in order to avoid the possibility that the moisture content of this surface layer might have approached air dryness. Analyses for exchangeable potassium were made on the soils in their original moist condition, after air drying, and again upon heating of the air-dry soils for 7 days at 105° C. The results obtained, expressed on the oven-dry basis in every case, are presented in table 19.

Moderate release of potassium appears to have taken place in several of the soils as a result of air-drying. However, in the most notable instance, that of soil No. 49-7, an Intrazonal Dark Magnesium Clay which gained 0.12 milliequivalent, release may be more apparent than real since satisfactory dispersion of this sticky, plastic clay in the original moist condition was not achieved. There is little evidence that fixation occurred upon drying.¹¹ Further changes of an

¹⁰b = 2.75, t = 5.54; and b = .24, t = 3.05, respectively.

¹¹ Some indications of potassium fixation in Hawaiian soils have been obtained by Volk (50) and Lyman (36).

TABLE 19. Effect of Air Drying and of Heating on Levels of Exchangeable Potassium in Soils.

Soil No.	Soil Group	Symbol	Land Use	Location	Exchangeable K — in m.e./100 gms.*		
					Moist	Air Dry	Oven Dry†
49-(2-5)	Low Humic Latosol	N1	Sugar Cane	Ewa	0.53	0.53	0.54
49-6	Gray Hydromorphic Soil	H1	Sugar Cane	Ewa	.31	.31	.37
49-7	Intrazonal Dark Magnesium Clay	M	Sugar Cane	Ewa	.50	.62	.97
49-8	Humic Ferruginous Latosol	T3	Grass	Upper Manawahua	.62	.60	.60
49-9	Humic Ferruginous Latosol	T1	Grass	Lower Manawahua	1.55	1.51	1.40
49-10	Alluvial Soil	V1	Sugar Cane	Halawa	1.69	1.63	1.60
49-22	Humic Latosol	A9	Forest	Tantalus	.44	.49	.49
49-23	Humic Latosol	A1	Grass	Upper Nuuanu	.099	.14	.16
49-24	Humic Ferruginous Latosol	T5	Pineapples	Upper Helemano	.26	.28	.26
49-25	Low Humic Latosol	N2	Sugar Cane	Makiki	.80	.80	.88
48-2	Humic Latosol	A5	Sugar Cane	Ookala	.45	.42
48-3	Humic Latosol	A5	Sugar Cane	Hakalau	.22	.20
48-11	Hydrol Humic Latosol	K6	Sugar Cane	Hilo	.16	.18

*Results expressed on oven-dry basis.

†Seven days at 105°C.

Analyses performed in part by H. H. Hagihara.

order similar to those resulting from air drying generally occurred upon heating the soils. An exception is soil No. 49-7, mentioned above, the exchangeable potassium content of which increased from 0.62 to 0.97 milliequivalent. Bray and De Turk (12) observed similar changes upon heating, and considered that the treatment does nothing more than facilitate or speed up the approach to a condition of equilibrium. Whether release or fixation takes place depends upon the equilibrium conditions existing prior to treatment.

GENERAL DISCUSSION

An opportunity is provided in the present study for a comparison of rates of release of non-exchangeable potassium upon cropping with those resulting from removal of exchangeable potassium followed by moist storage. It will be appropriate for this purpose to consider the soils from which all of the exchangeable potassium was removed and which were subsequently stored in the hydrogen-saturated condition. Comparison of the respective values shown in tables 7 and 15 indicates that release upon cropping was from 3.2 to 9.6 (average 7.5) times as great as release upon moist storage. The contrast is even more striking when it is realized that the cropped soils were in fallow during 14 months of the period upon which the comparison is based.

The reason for this pronounced biological influence upon the rate of release of non-exchangeable potassium is not apparent. The effect of growing plants upon the availability of soil nutrients is frequently attributed to acidity resulting from the release of carbon dioxide by plant roots. It seems improbable, however, that such release could, under the conditions of the experiment, result in a more acid condition than that produced by the substitution of hydrogen for the exchangeable bases of the soil. As a matter of fact, it was found in a side test relative to the moist storage of the soils that deliberate failure to remove all of the hydrochloric acid with which the soils were leached preparatory to storage produced no measurable effect upon the subsequent release of potassium. It may be pointed out in this connection that Joffe and Levine (32) observed no release of *fixed* potassium upon continuous treatment with carbon dioxide. Chandler, Peech, and Chang (14) point out the possibility that plants may feed directly upon non-exchangeable potassium.

A possible explanation involves the concept of equilibrium and the law of mass action. As is well known, plant roots, under certain conditions, are capable of absorbing potassium from solutions containing extremely low concentrations of this nutrient. The roots of the potassium-starved plants may therefore be thought of as withdrawing potassium from the soil solution about as fast as it is released. This action, together with the probable uptake of other constituents of the crystal lattice, such as magnesium and silicon, might be expected to produce a pronounced weathering effect upon the potassium minerals and a consequent enhanced release of non-exchangeable potassium. Such action would be absent in the stored soils, except insofar as the tightly held hydrogen on the clay was replaced by cations resulting from weathering. Possible support for the above concept is found in a study by Peech and Bradfield (44), who observed that one and a half times as much potassium was released by a biotite-clay mixture at pH 6.87 as by biotite in water at the same pH . They attributed the more rapid release to the removal of hydrolysed potassium from the solution by the clay. A similar effect has been noted by Hall (22) relative to electro dialysis

of potassium minerals, namely, that the presence of an electric field enhances the escape from the crystal of potassium ions that have gone into solution.

Tending toward more rapid release of non-exchangeable potassium in the stored soils, however, is the fact that levels of exchangeable potassium were lower in these soils than in the cropped soils. It is necessary to remember, however, that values for exchangeable potassium represent *average* values for the soil as a whole, and that micro levels of exchangeable potassium at points of contact between soil particles and absorbing root surfaces are presumably far below average values. Moreover, if the "contact exchange" views of Jenny and Overstreet (28, 29) are accepted, it is possible to visualize absorption of potassium by roots from weathered surfaces of potassium minerals independently of the soil-solution-soil-mineral equilibrium.

One would expect, upon the basis of the foregoing discussion, that the rate of liberation of potassium upon electro dialysis would correspond more nearly to that realized upon cropping than to that resulting from moist storage of H-soils. Comparison is made difficult by the fact that different periods of time are involved. However, taking the data corresponding to 30 days of electro dialysis, it is found that the rate of release of potassium by this method, although less than that upon cropping, was greater with a single exception than that resulting from moist storage of H-soils. A longer period of electro dialysis would have narrowed the gap between release upon cropping and electro dialysis and widened that between release upon electro dialysis and moist storage of H-soils. The Hydrol Humic Latosol, No. 44-26, although releasing large quantities of potassium upon cropping, proved very resistant to the influence of the imposed electric field.

Reasoning similar to that employed in the preceding discussion might be invoked to account for the more rapid release of non-exchangeable potassium in the Ca-soils than in the H-soils when these were stored in the moist condition. We may think of the potassium minerals as being in intimate contact with the exchange material of the soil and even entering into exchange reactions themselves by virtue of exchange positions on partially weathered surfaces. Now, as potassium is released, it must be adsorbed in part on exchange surfaces and the more completely such adsorption takes place, the more rapid should be the release of potassium. Finally, the energy of adsorption of calcium is less than that of hydrogen and the ability of Ca-soils to take up potassium, therefore, greater than that of H-soils. Accordingly more rapid release of non-exchangeable potassium would be expected where calcium was the complimentary cation. Jenny and Reitemeier (30) obtained symmetry values of 14.5 and 28.8 as a result of treating H-clay and Ca-clay with ammonium and potassium ions, respectively. The two ions possess similar energies of adsorption.

On the above basis greater release of potassium would occur in soils from which all of the exchangeable cations had been replaced with calcium than where replacement was only partial. This is in accordance with the data (cf., tables 6 and 8).

Failure of calcium to effect release of non-exchangeable potassium when added as calcium hydroxide to soils from which no part of the exchangeable potassium or other exchangeable cations had been removed prior to moist storage (cf., table 9) may be accounted for in part at least as follows: In the first place, the period of storage was relatively brief, 6 months as compared

with 40 and 41 months for the treatments already considered. Secondly, the quantities of calcium added as the hydroxide to the untreated soils were relatively small, final pH values except in one instance not approximating corresponding values of the calcium acetate-treated soils. Finally, soil-solution and exchangeable potassium and other cations were allowed to remain in the soil. This would result in a competition between these cations and potassium released from non-exchangeable sources for positions on exchange surfaces occupied by added calcium. This would be expected to reduce greatly the liberating influence of the treatment.

Both the cropping and moist storage techniques for the measurement of release of potassium are, of course, empirical in that they bear no known relationship to release under field conditions. In view of the tremendous influence of growing plants upon the rate of release observed in the present study, it would appear that of the two procedures, cropping most nearly approaches conditions obtaining in the field.¹² However, conditions in pot and field are far from parallel and extrapolation to field conditions should be made with caution. For example, we cannot picture levels of exchangeable potassium in field soils being reduced from 1.00 to 0.15 milliequivalent per 100 grams of soil in the course of 5½ months, as happened in some of the potted soils. No more can we expect release of potassium per unit weight of soil in the field to be of the order of that which was obtained in pots. Moreover, release of non-exchangeable potassium is a function of the crop, as has been shown by Evans and Attoe (17) and others. The ability of sugar cane to foster the release of non-exchangeable potassium differs in all probability from the corresponding abilities of Sudan and panicum grasses.

A number of concepts have been advanced to account for the presence of releasable non-exchangeable potassium in soil. In a recent paper, van der Marel (49) suggests that the potassium-supplying power of *tropical* soils is the result of rapid weathering, particularly of the mineral biotite. He observes that in the more weathered soils where little of this mineral is present potassium deficiency is frequently in evidence. Although climatic conditions in many parts of Hawaii are certainly conducive to intensive weathering, which would suggest less resistant primary potassium minerals as the source, in part, of the released non-exchangeable potassium in some Island soils, the answer must be sought elsewhere. Petrographic study of Hawaiian soil minerals by Hough and Byers (25) has shown that many Island soils are weathered to the point where the only remaining unweathered minerals are illmenite and magnetite.

Attoe and Truog (4) and others have suggested fixed potassium as a source of non-exchangeable potassium capable of release. Although fixed potassium may well be present in some of the less well drained and less weathered sugar cane soils, the character of which is little understood, it is doubtful that this could account for much of the release in soils which are essentially kaolinitic and oxidic in character.

Illite, a secondary potassium mineral described by Bray (11) and which is only moderately resistant to weathering, has been proposed to account for the

¹² It has been shown, however, that the quantities of potassium liberated by the two methods are related.

liberation of potassium in Illinois soils. Opinions regarding the presence of illite in tropical soils are at variance. Nagelschmidt (42), among others, is of the opinion that it is not commonly a constituent of soils of the "wet tropics." Recently, however, Caillere, Betremioux, and Henin (13) found by X-ray analysis that illite is present in some of the more fertile of the kaolinitic soils of Africa. The presence of illite has in fact been established in Hawaiian ceramic clays by Wentworth, Wells, and Allen (55). However, the fact that illite is a constituent of these clays does not establish its presence in the sugar cane soils of the Islands. Hawaiian ceramic clays are formed at elevations of several thousand feet where temperatures are low, as measured by tropical standards, where rainfall is high, and drainage impeded. Soils devoted to sugar cane, on the other hand, are at lower elevations where temperatures are higher and rainfall is more moderate, and, on the residual soils at least, drainage is generally good. In some of the poorly drained soils the picture is more obscure. Although the nature of the clay mineral or minerals is unknown, colloidal separates of many Hawaiian soils contain substantial amounts of potassium, as has been shown by studies of Hough and Byers (25), Hough, Gile, and Foster (26), and, more recently, by Tanada and Dean.¹³ Moreover, it is probable that in the more weathered soils most, if not all, of the potassium is in the colloidal fraction. It seems likely that this fraction is the principal source of the potassium released in Hawaiian soils.

The more rapid initial release of non-exchangeable potassium, whether upon cropping, moist storage, or electro dialysis, implies that this fraction of the soil potassium is not all convertible with equal facility into the exchangeable form. This is particularly apparent upon examination of the electro dialysis curves in figure 8. The more rapidly liberated potassium may be presumed to consist of that held on or near more or less weathered surfaces of potassium minerals and possibly of fixed potassium. The more slowly released fraction, exemplified by the moderately sloping portions of the curves, is presumably derived from weathering of potassium minerals whereby fresh surfaces of the crystal lattice are continually exposed.

It was noted that levels of exchangeable potassium in the untreated soils and rates of release of potassium were directly related. This was true both of release upon moist storage and of release upon cropping. It may be said, therefore, that levels of exchangeable potassium in the untreated soils reflect potential rates of release of potassium. Such relationships would be expected only if the soils were in equilibrium with respect to exchangeable potassium, as indeed these soils were shown to be. Attainment of equilibriums in similar periods of time, following displacement of exchangeable potassium, are suggested by the above relationship since equilibrium levels are manifestly functions of time as well as of rates of release.

Presence of a state of equilibrium in soils which have suffered no treatment other than air drying after leaving the field suggests the existence in the field at the time the samples were taken of a condition which approaches equilibrium. Several factors may be cited to account, in part, at least, for this condition.

¹³ Unpublished data in files of Department of Chemistry and Soils, Hawaii Agricultural Experiment Station.

As we have already seen, plants can obtain potassium from non-exchangeable sources in the presence of the exchangeable form and accordingly the latter may not be severely displaced at any time in the crop cycle. Moreover, it will be recalled that soil samples for the release experiments were taken shortly after the cane was harvested, which normally would mean that potassium fertilizer, where used, had not been applied for at least a year.¹⁴ In addition, uptake of potassium by sugar cane diminishes with approaching maturity. It should not seem surprising, therefore, to find at harvest, or shortly thereafter, a condition approximating a stable state.

In light of the results of this study and of those of many other workers, the over-all picture of potassium fertility in Hawaiian soils may be summarized as follows. Small quantities of potassium which are completely and instantly available to sugar cane roots exist in the soil solution. Very much larger quantities of potassium which are in instantaneous equilibrium with potassium in the soil solution are held by the exchange materials of the soil. Soil solution and exchangeable potassium together thus comprise the potassium which is available to the crop at a given instant. That these forms of potassium are readily available to plants was shown in figure 1 and table 12 by the rapid decreases in exchangeable potassium where levels were initially high and where potassium fertilizer was not added. Supplies of such potassium in Hawaiian sugar cane soils generally range from 100 to 2,000 pounds K_2O in the surface foot of soil. Considerably larger amounts are present in isolated cases.

As the level of exchangeable potassium is lowered through cropping below the equilibrium level, further potassium is slowly converted from the non-exchangeable to the exchangeable form. The rate of this release depends upon the extent of the displacement of exchangeable potassium below the equilibrium level, upon the amount and nature of the reserves of non-exchangeable potassium, and upon the degree of base saturation of the soil. Doubtless other factors, including the variety of cane and the physical condition of the soil, are also involved.

The quantity of potassium available to the sugar cane crop is, therefore, not measured alone by the amount of exchangeable potassium present in the soil at the start of the crop but includes also that which becomes available in the course of the crop.¹⁵ At equilibrium, a state probably most closely approached shortly after harvest, the level of exchangeable potassium reflects the ability of the soil to maintain the supply of this nutrient through release of non-exchangeable potassium. The point at which this level should be maintained through application of potassium fertilizer (in order to insure an adequate supply of the nutrient at all times and yet avoid waste of potassium through luxury absorption and leaching, both of which tend to mount with increasing level of exchangeable potassium) depends upon both soil and climatic conditions.

¹⁴ Cane crops are ordinarily grown in Hawaii for periods ranging from about 14 to 24 months.

¹⁵ Potassium present in the soil solution is included in the analysis for exchangeable potassium.

SUMMARY

A 4-year study was made of the release of non-exchangeable potassium in Hawaiian sugar cane soils. Methods of approach to the problem comprised (1) intensive cropping of 12 soils in pots with Sudan and panicum grasses, and (2) partial and complete removal of exchangeable potassium by chemical means from 26 soils, followed by moist storage for 41 months. Soils were stored both as H-soils and as Ca-soils. The possibility of employing electro dialysis and acid extraction for determining rates of release of non-exchangeable potassium was investigated. A study was made of the influence of air drying and of oven drying upon the release of potassium in soils. Results of the study may be summarized as follows:

1. Moist storage of soils, untreated except for previous air drying, for 42 months produced no changes of consequence in levels of exchangeable potassium.

2. Partial removal of exchangeable potassium, followed by moist storage, resulted in the release of small amounts of potassium.

3. More potassium was released upon moist storage in soils from which all exchangeable potassium had been removed than where removal was only partial.

4. Ca-soils liberated two and a half times as much potassium on moist storage as H-soils.

5. Liming of acid soils up to 4 tons CaO per acre, followed by moist storage, did not result in the release of potassium if exchangeable potassium were not first displaced.

6. Treatment of soils with hydrogen peroxide to destroy organic matter did not result in increased recovery of exchangeable potassium.

7. Levels of exchangeable potassium diminished rapidly as a result of cropping, becoming generally constant at values less than 0.1 milliequivalent per 100 grams.

8. Levels of potassium in the first two crops (combined) were directly related to initial levels of exchangeable potassium in the soils.

9. Release of potassium upon cropping averaged approximately 700 pounds K_2O per acre-foot of soil for seven crops (42 months including 14 months of fallow).

10. Liberation of potassium upon cropping exceeded release on moist storage of H-soils by approximately seven and a half times. However, rates of release by the two methods were directly related.

11. Release of potassium, both upon cropping and upon moist storage, was directly related to initial levels of exchangeable potassium. This was taken to indicate that, at equilibrium, levels of exchangeable potassium reflect potential rates of release.

12. Uptake of exchangeable potassium by seven crops amounted to about 80 percent, on the average, of quantities initially present.

13. Release of potassium upon moist storage was more rapid in less weathered than in more weathered soils.

14. Non-exchangeable potassium constituted from 45 to 90 percent (average 65 percent) of the total quantities of potassium absorbed by the crops.

15. Non-exchangeable potassium taken up by the crops averaged 6.2 percent of the total quantities of potassium present in the soils at the beginning of the experiment.

16. Large amounts of non-exchangeable potassium were taken up by plants in the presence of substantial quantities of exchangeable potassium.

17. Electrodialysis for periods of 30 days resulted in recoveries of non-exchangeable potassium ranging roughly from 25 to 1,300 pounds K_2O per acre.

18. Release of non-exchangeable potassium upon electrodialysis was directly related to release by H-soils on moist storage.

19. Rates of release of potassium, whether upon moist storage, cropping, or electrodialysis, decreased with time.

20. Extraction of exchangeable potassium-free soils with hot normal hydrochloric acid produced quantities of potassium which were directly related to the release of non-exchangeable potassium upon cropping and also upon moist storage.

21. Moderate release of non-exchangeable potassium resulted in a few instances as a result of air drying and of oven drying moist field soils.

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