

AN ABSTRACT OF THE THESIS OF

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(Name) (Degree) (Major)

Date thesis is presented: April 19, 1963

Title CHEMICAL PROPERTIES OF SOILS RELATED TO SEASONAL
FLUCTUATIONS IN EXCHANGEABLE POTASSIUM

Redacted for Privacy

Abstract approved _____
(Major professor)

Representative sites of the Dayton, Woodburn, Jory, Quillayute, Astoria, Willamette, Walla Walla, Deschutes, Laki and Owyhee soil series were investigated for seasonal changes in exchangeable potassium in air dry samples. No consistent seasonal variations were found which could be attributed to wetting and drying in the field. Cropping reduced the air dry exchangeable K in some soils as the growing season progressed.

The laboratory analysis of exchangeable potassium in the Dayton soil was found to be affected by the physical nature of the extracting procedure. Changes in the shaking time, surface tension of the extractant, or temperature of the extractant resulted in different exchangeable K values. The differences between air- or oven-dried soil and moist soil were also affected by these physical factors.

The differences between the two moisture levels were not wholly attributed to potassium fixation and release. The possibility of negative errors in the exchangeable K determination was pointed out.

CHEMICAL PROPERTIES OF SOILS RELATED TO SEASONAL
FLUCTUATIONS IN EXCHANGEABLE POTASSIUM

by

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A THESIS

submitted to

OREGON STATE UNIVERSITY

in partial fulfillment of
the requirements for the
degree of

MASTER OF SCIENCE

June 1963

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Redacted for Privacy

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Date thesis is presented: April 19, 1963

Typed by Jolene Wuest

ACKNOWLEDGMENT

The author gratefully acknowledges the advice and assistance offered by Dr. L. A. Alban throughout this research program and in the preparation of the manuscript. The author also expresses gratitude to Dr. M. E. Harward for reviewing the manuscript and his helpful advice.

The author also acknowledges the Oregon State Agricultural Experiment Station and the American Potash Institute for their cooperative financial assistance.

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CHEMICAL PROPERTIES OF SOILS RELATED TO SEASONAL FLUCTUATIONS IN EXCHANGEABLE POTASSIUM

INTRODUCTION

Soil science, and fertility in particular, falls into a class for which basic principles are scarce. Nevertheless, a significant crop response can probably be considered a basic principle underlying fertility studies, one which may become difficult to manage when a number of variables are present. One of these variables which is evaluated by soil testing is the nutrient level of a soil and the need for fertilization. This then is the role soil testing plays in a fertility program and it is generally carried out in two steps, the analysis itself and the interpretation or fertilizer recommendation.

The soil test has become widely used as a basis on which fertilizer recommendations are made; nevertheless, the role of the field man in interpreting the results of an analysis is a large and important part of the overall program. It is necessary to keep this fact in mind when considering soil testing procedures themselves, which must be applicable to routine analysis. The actual relationship of any particular soil test value to the level of that nutrient, in terms of its availability to a particular crop, must be understood by the person who makes the recommendation. This thesis attempts to show some of the inherent variability of exchangeable potassium values as

used in a soil testing procedure. The fact that such variability is present under certain conditions does not devalue the usefulness of exchangeable potassium values, but it does necessitate an understanding of these fluctuations in order to make accurate fertilizer recommendations based on exchangeable levels. It is hoped that this thesis will give some insight into this problem, not necessarily by producing rigorous data and procedures, but rather by giving a logical interpretation of the variability which is often encountered in exchangeable potassium values.

There have been other methods proposed for evaluating soil potassium, most of which are aimed at measuring the soil's supplying power or natural capacity to release potassium to plants. Most of these procedures, except possibly nitric acid solution, are not easily done on a routine basis. In certain cases these methods may be a better evaluation of the potassium status of the soil than the exchangeable cation. If exchangeable potassium alone is to be used, then it becomes necessary to fully understand its meaning in order to apply it accurately in all cases. On soils where fertilization and heavy crop removal are involved the exchangeable value is a good indicator of past management and much more sensitive than supplying power.

Measurement of exchangeable potassium can be done either with field moist or air dry samples but the two results in most cases

are not the same. The present soil testing procedures use air dry methods exclusively. The difference between the two values has been attributed to potassium fixation or release. The magnitude of the difference between the moist and dry analysis is not easily predicted from clay mineral data. It has been stated that exchangeable potassium should be evaluated from a field moist sample since this is indeed the condition of the soil in which the plant is always found. Also the consistent use of air dry values has been suggested. This thesis does not attempt to resolve this question in its entirety, although some data are presented showing the difference between the two results. The accurate interpretation of the soil test and the relationship of the resulting fertilizer recommendations to overall management practices is usually more critical than small differences in the soil test values themselves.

One further question about air dry exchangeable potassium is whether it has a seasonal fluctuation, as might be expected from the nature of the equilibrium reactions which establish the potassium distribution in the soil colloid system. It is necessary to know whether samples taken in the spring or late fall when the soil is wet can be used to evaluate the summer levels when the soil is dry. This subject is the major topic of this thesis. Seasonal fluctuations will be used to point up a number of the characteristics of exchangeable

potassium which are related to other chemical properties of the soil.

These characteristics are important when using the exchangeable cation for evaluating the nutrient status of potassium.

LITERATURE REVIEW

A recent paper which reports changes in exchangeable K during a growing season is one by Grava et al. (5). The soil used was the Nicollet clay loam and an increase of exchangeable potassium and phosphorous was observed in every case as the soil changed from moist or air dry to an oven dry state. The most rapid increases occurred within the last ten percent of moisture release. This latter effect is mentioned by Scott and Smith (18) in their paper in which they show a doubling of the exchangeable K values between five percent moisture and oven dry, and only small changes between five percent and higher moisture contents. Grava's data, mentioned above, also indicate decreases in field moist exchangeable potassium as the growing season progresses, and a similar but less pronounced decrease when oven dry K is used. However the air dry values only show up a seasonal trend in that the lower the moisture content of the air dry samples the closer the air dry curve approaches the oven dry. The lowest field moisture was only 23 percent. This seasonal trend is undoubtedly related to crop removal. Unless the crop removal has overshadowed any release mechanism, the soil should have increased in exchangeable potassium as it dried, in the same way as was observed in the laboratory.

Hanway and Scott (8) show a high correlation between the potassium extracted by 1N ammonium acetate and both 0.5N and 0.1N hydrochloric acid. The ten soils examined all showed an increase upon drying and then some decrease again upon rewetting for 24 hours. The subsoils showed higher oven dry values and lower moist values than the surface soils, and also a greater change upon rewetting. In a previous paper Scott, Hanway, and Stickney (17) had reported similar results which showed that, a) soils with a low K level increased upon drying, b) KCl treated soils decreased upon drying, and c) soils of an intermediate K level decreased on drying to five percent moisture followed by an increase with further drying. These authors could not explain why increasing additions of hydrogen, sodium or ammonium chlorides and subsequent oven drying reduced the release of potassium to 1N ammonium acetate. C. E. Marshall states (11) that Ca and Mg clays show by far the greatest amount of water adsorption, then K-clays, H-clay, Na-clay, and least of all NH_4 -clay.

From the above discussion it appears possible that if oven drying removed some of the water of hydration from the cations used to saturate the soils, rehydration would occur at decreasing rates going from H to Na to NH_4 . The rates of exchange would be reduced in the same order, if complete rehydration of the colloid

surface is necessary for complete exchange to take place. The fact that calcium presaturation produced no such reduction would also support this theory. It is inferred that the exchange surface of a dried soil may not rewet immediately upon addition of the exchanging solution due to slow movement of vapor onto the exchange surface.

If fine capillary pores exhibit the same wetting phenomenon as has been observed and described in soils as capillary conductivity, then it can be stated (3): "that the capillary conductivity of a soil is practically zero at moisture contents lower than that of the wetting front, since there is no continuity of moisture films." Wetting of a dry soil sample must be closely associated with the hydration of the colloid surfaces by vapor and the rate at which it occurs. Water always moves from a higher to a lower vapor pressure region and the vapor pressure of water is inversely proportional to the radius of curvature of the surface. This affect of pore size upon the vapor pressure is governed by the equation $\ln P/P_0 = 2\gamma M/r\rho RT$.^{1/} (Kelvin Equation). Rewetting of organic matter would also be expected to be slow and related to the adsorbed cations. The amount of the total colloidal surface which can be wetted in a short time for one particular soil should be

^{1/}

γ = surface tension, M = molecular weight, r = radius of curvature
 ρ = density of water, R = gas content, T = absolute temperature,
 P_0 = vapor pressure of free water surface, P = vapor pressure of
a surface with radius of curvature r .

greater the finer the total pore space, the lower the organic matter and non-expanding mineral contents, the higher the temperature and the lower the surface tension of the exchanging solution. These relationships could then be applied to explain anomalous decreases or no change of exchangeable K upon drying, in soils which would be expected to exhibit increases.

One way of testing this hypothesis is by considering the differences in release characteristics between surface soils and subsoils upon drying or upon rewetting. Two major physical differences which occur in many soils with increasing depth are a lower organic matter content and a higher clay content and therefore smaller pore size. Profile descriptions also reported by Hanway and Scott (7) show a positive relationship between clay content vs air dry or oven dry exchangeable K, especially for the soil Edina #32 in which a clay layer occurs. Also the reversion on rewetting was the least and the slowest in the surface soils, and occurred only in oven dried samples. The most recent data by Hanway, et al. (9) show a distinct difference between silt loam soils and sandy loam soils in their profile description of exchangeable K as determined on field moist and oven dried samples. Generally there was only a slight increase in exchangeable K or sometimes a decrease at the surface, upon drying a sandy soil. The heavier textured soils showed their greatest increases at

depths below one foot. Carter (4) reported that he observed increases in exchangeable K with drying for all horizons of the soils he used, except the surface soils Nehalem A_{1p}, Tillamook A_p, Dayton A₁₁ and Cascade A_p and all horizons of Walla Walla. These surface horizons just mentioned ranged in organic matter from four to eight percent and the Walla Walla contained from 30 - 44 percent sand. In most cases the clay content is in turn correlated with the C. E. C. and therefore horizons high in clay may also be high in potassium on a me/100g basis.

Returning to the results mentioned earlier of the effect of previous cation saturation and oven drying upon release of potassium to 1N NH₄Ac, it seems possible to make a refinement in the explanation by considering a paper on cesium sorption by Tamura and Jacobs (19). They showed that air and oven drying increased the cesium sorption capacity of vermiculite and to a lesser extent montmorillonite, from 6N NaNO₃ containing about 10⁻⁴ moles cesium per liter. The same authors reported (10) that small amounts of previous K saturation resulted in increased cesium sorption from dilute cesium solutions. A soil containing 0.50 me/100g of K which is equilibrated with 1N NH₄Ac at a 1:10 dilution would have a solution concentration of 0.5 me/liter or 5 x 10⁻⁴ moles/liter. This range of K solution concentrations would be expected to react similarly to both the dilute

and 6N NaNO_3 Cs solutions mentioned above. It follows that potassium sorption from an exchanging solution would be increased by oven drying, particularly whenever vermiculite is present. Depending on the importance of this effect it would enhance the magnitude of the fixation as measured by exchange procedures.

Matthews and Sherrel (12) observed that the percent K saturation necessary to produce fixation was $1.11 \pm .12$ for the 360 soil samples used. Hanway, et al. (9) also mentioned that samples from field replicates low in exchangeable K showed an increase from drying, whereas those from replicates high in exchangeable K showed a decrease from drying. It is not clear how these results are related to the fixation and release mechanism but they may fit in with the specific adsorption mentioned in the previous paragraph.

Now let us consider the other end of the moisture range, the field moist condition. In all the literature mentioned, the method of determining field moist values is never questioned nor is there much information available which deals with the measurement of field moist values by different methods. Many different correlations have been made between field moist results and other moisture levels or various plant parameters. These correlations generally show that exchangeable K increases on drying and also that field moist K is often a good measure of availability to the plant, as stated by Barber,

et al. (2). Based upon the previous discussion the most apparent advantage of moist exchangeable K is that wetting difficulties would be overcome more easily. If wetting, then, was the only deterrent to complete exchange one would expect moist K values to be greater than dry K values, depending upon the importance of wetting in any particular soil sample. However, generally the opposite relationship between moist and dry samples is observed. Therefore, a further explanation must be sought. A procedure which is closely related to the determination of exchangeable cations is the determination of cation exchange capacity. It would seem that the determination of exchangeable K would be subject at all times to the same inherent errors as are described by Okazaki, Smith and Moodie (13) for the replacement of native exchangeable cations, and also under field moist condition to the errors involved in replacement of the adsorbed index ion. Eight 30-ml increments of saturating solution were required to completely saturate 5-g samples of soils with exchange capacities over about 25 me/100g, and six 30-ml increments of replacing solution were used to replace applied barium. Results from treatments which were not as complete as these would be subject to greater variations between soils. Rarely, if ever, are routine exchangeable cation determinations carried out in such a manner that one would expect complete exchange and therefore they may be subject to soil variations. It is difficult

to differentiate between an incomplete exchange reaction due either to incomplete replacement at the colloid surface or to incomplete equilibrium between the internal solution within the soil pores and the external solution phase. However it is unlikely that the former effect would be altered by drying since the same symmetry concentrations are used for exchange at both moisture levels. The latter effect would be different at the two moisture levels. If the water in a moist soil is held and not free to equilibrate with the external solution, then the soil water is held so as to form a separate phase at the start of equilibration.

It seems that water stable aggregates would be necessary for the retention of water in the manner stated above. Baver (3) states: "It is a well-observed fact that organic matter must be made soluble or oxidized to ensure complete dispersion of soils. The polar adsorption of organic matter not only is a factor in reducing the exchange capacity of the organic colloid but also probably impedes the exchange of those cations associated with the inorganic colloids." The movement of water out of these aggregates would be the same as the movement of water in saturated soils according to Darcy's law, which states that the velocity of flow is directly proportional to the difference in pressure head and inversely proportional to the length of movement. Since no pressure head exists to move the water

out of these aggregates it will remain there throughout equilibrium. The movement of ions between these two phases would have to occur by a simple or some more complex diffusion process, which would be subject to time and temperature variables.

In summary, it appears logical that the physical properties of the soil may play a part in determining the rate of exchange or equilibrium which occurs between the colloidal surface and the external solution in both moist and dry soil samples, although few workers have reported any correlations of this type. Almost all changes in exchangeable potassium in all situations have been explained by or attributed to "release" or "fixation" mechanisms, although no such mechanisms have been clearly proven except in the case of inter-layer entrapment. ^{2/}

^{2/} For a recent and rather thorough coverage of mechanisms, and release and fixation characteristics of clay minerals the reader is referred to the Ph. D. dissertation of G. E. Richards (16).

MATERIALS AND METHODS

Field Samples

Field samples were obtained from two sources: first, samples taken in the Willamette Valley and Tillamook area which included the Dayton, Woodburn, Jory and Quillayute soil series; secondly, samples supplied by Branch Experiment Stations in Oregon which included the Astoria, Willamette, Walla Walla, Deschutes, Laki and Owyhee soil series. Composite soil samples were taken from plots not larger than 20 by 20 feet every two months on each soil series. In some cases cropped and fallow plots were maintained side by side. The crop generally consisted of grass or alfalfa. The individual sites were chosen, as closely as possible, to represent the different soil series. No fertilization occurred during the period of sampling on any sites.

Soil Test Analysis

All the data reported as seasonal fluctuations in exchangeable K and changes in exchangeable K and Ca upon drying was obtained by extraction with 1 N H_4Ac and determined with the flamephotometer. Cation exchange capacity, organic matter and pH were determined by NH_4Ac saturation, Walkley-Black method and a 1:2 soil-water

dilution, respectively (1). Oven drying was at 105°C.

Laboratory Analysis of the Dayton Soil

All exchangeable potassium results were obtained by equilibration of two grams of soil with 20 ml of 1N NH_4Ac for either 30 minutes or 24 hours, centrifuging and subsequent analysis of the supernatant by the same routine procedures as mentioned above.

Where a wetting agent was used, enough was added to the extractant to give a 0.1 percent solution. The surface agent was Triton X-155 (15) which is a non-ionic alkyl aryl polyether alcohol and reduces the surface tension of distilled water at this concentration to 30 dynes/cm at 25°C. Where heat was used, the extractant was measured out and then heated to 80 - 90°C in a stoppered tube to prevent evaporation. The soil sample was then added and the tube shaken for 30 minutes.

Various moisture contents were obtained by air drying a saturated sample from the field for different periods of time, followed by storage in weighing bottles for a few days before using. All moisture contents were based on 24 hour drying at 105°C.

Mechanical analysis of the two Dayton samples was done by duplicate pipette analysis using the routing procedure of the Soil

Physics Laboratory at Oregon State University.

X-ray Diffraction Analysis

Air dried samples were treated with H_2O_2 without heating until no further reaction was apparent, the sand fraction was removed by centrifuging, and the remaining suspension was Ca saturated and washed. No free carbonates were expected in the surface soils used as indicated by pH. Part of the Ca-soil was then K saturated and washed. The resulting Ca and K saturated samples were applied in duplicate to glass slides with a spatula and dried at room temperature. After these slides were X-rayed the Ca slides were solvated with glycol by heating for an hour at $65^{\circ}C$ and storage overnight in a closed container, while the K slides were heated at $500^{\circ}C$ and then both sets were re-examined. By shifts in the peaks of the patterns with these different treatments, the clay minerals were determined as given in Table 1 by the criteria explained in Grim's book on clay mineralogy (6). The pattern for the Dayton surface soil prepared in this manner is given in Figure 1.

It is believed that adequate clay mineral descriptions of the soils were obtained by this rather simple procedure, for fertility correlations. The exact identification of the type and amount of clay minerals present would probably require more delineative

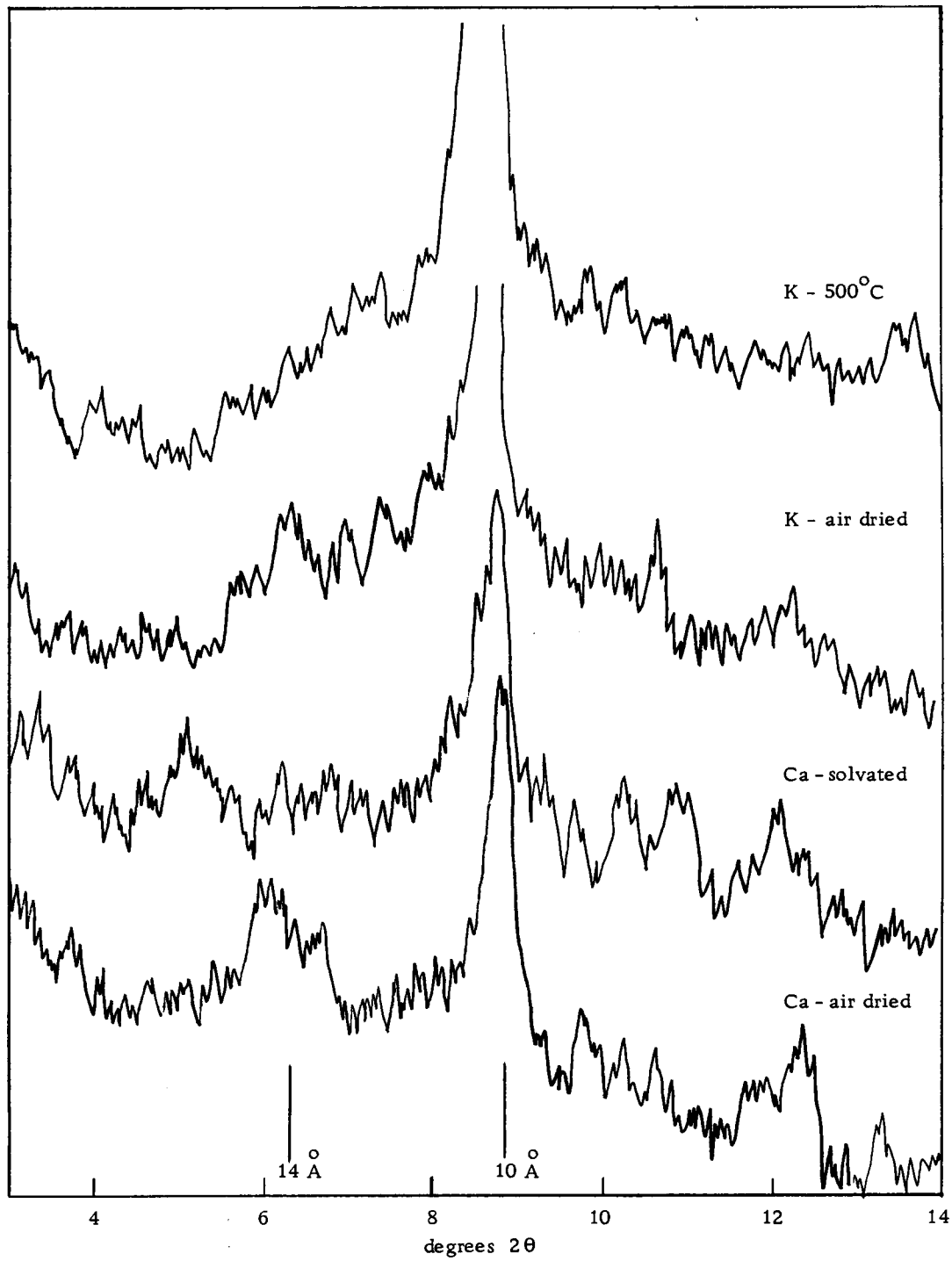


Figure 1. X-ray Diffraction Patterns for the Dayton Surface Soil.

pretreatments. No X-ray patterns were distinguishable for any of the treatments of the Deschutes and Laki soils. This inability to differentiate a pattern may be related to the nature of the parent materials from which these two soils are derived. The former is derived from pumice parent materials and the latter from imperfectly drained peat and alluvial deposits high in organic matter.^{3/}

Table 1. Some Chemical Properties and Clay Mineral Interpretations of Surface Soils.

Soil Series **	pH	C. E. C. me/100 g	Clay Minerals* (in order of peak intensities)
Astoria	5.5	26.4	M, (V), I, Int
Deschutes	6.1	11.7	non-diffracting
Dayton	4.8	14.1	I, M
Quillayute	5.9	50.5	M, (V), Int, I(K)
Woodburn	5.5	14.5	I, M, (K)
Willamette	5.7	16.8	Int, I, (K)
Owyhee	7.0	22.2	I, Int, (V)
Laki	6.7	9.9	non-diffracting
Walla Walla	6.6	17.1	I, (Int)
Jory 506 ***	5.4	22.1	Int, (Ch, K) (I)
508	5.3	23.2	Int, (Ch, K) (I)
510	6.1	20.7	Int, (Ch, K) (I)

*I = illite, V = Vermiculite, M = montmorillonoid, Ch = chlorite, K = kaolin, Int - chloritized integrate, () = possibly present.

** Soil series designations were either established previously or supplied by Dr. G. E. Simonson, OSU, or local Soil Conservation Service personnel.

*** Numbers refer to different cooperative TVA experiments.

^{3/} From the profile descriptions supplied by A. E. Gross, Supt. of Klamath Experiment Station.

RESULTS AND DISCUSSION

Seasonal Fluctuations in Exchangeable K

Table 2 contains the exchangeable K analysis of air dry samples taken every two months on ten different soil series. These soils represent areas which cover a fairly wide range of climatic conditions with respect to seasonal wetting and drying and also a wide range of exchangeable potassium. In most of Oregon only a small percentage of the annual rainfall occurs in the summer months, and soil moisture decreases considerably. It is difficult to analyze how much of the difference between samples is due to sampling variation between months and how much can be attributed to seasonal changes. What variations would be expected to arise as a result of seasonal changes, and at what relative rates would they occur?

In general the soils from the 0" - 3" depths showed higher values than the 3" - 8" depth. This is attributed to the greater amount of organic matter in the former, since in no cases were the type of clay minerals or the air dry moisture contents appreciably different between the two depths.

There was no indication of a seasonal fluctuation due to wetting and drying per se for all the soils studied. Since the '61-'62 season was not anomalous with respect to rainfall there is no reason

Table 2. Seasonal Fluctuation in Exchangeable K. *

Soil Series and Plots		Sampling Date							
		10/61	12/61	2/62	4/62	6/62	8/62	10/62	12/62
Astoria**		Millequivalents per 100 grams							
C	3	1.34	1.45	1.26	1.21	1.38	1.44	1.44	1.46
	8	.93	1.25	.94	.95	1.33	1.14	1.21	.86
F	3	1.23	(2.21)	1.12	.98	1.35	1.17	1.27	1.80
	8	.81	1.00	.77	.90	.97	.94	1.11	.86
Deschutes									
C	3	1.09	.93		1.17	1.44	1.06	1.44	.96
	8	.66	.85		.86	1.38	1.29	.60	.64
F	3	.82	1.03		1.29	1.57	.87	.96	.96
	8	.77	.80		1.59	1.70	.46	.51	.62
Dayton									
C	3	.53	.52	.50	.42	.38	.25	.41	.28
	8	.23	.26	.27	.34	.28	.23	.24	.19
F	3	.59	.50	.52	.50	.50	.43	.50	.50
	8	.33	.34	.36	.40	.32	.37	.40	.36
Quillayute									
C	3	.66		.80	.99	.83	.69	(1.50)	.50
	8	.46		.44	.48	.48	.41	.64	.40
F	3	.51		.52	.58	.44	.41	.58	.42
	8	.44		.44	.38	.42	.35	.48	.36
Woodburn									
C	3	.69	.78	.70	.75	.74	.73	.68	.72
	8	.49	.50	.57	.54	.56	.67	.51	.48
F	3	.57	.71	.68	.68	.65	.64	.73	.58
	8	.50	.58	.60	.56	.54	.51	.58	.52
Willamette									
C	3		.98		.96	1.00	1.17	1.01	.96
	8		.72		.94	.74	.76	.70	.64
F	3	.85	1.00		.82	1.03	.94	.91	.89
	8	.78	.88		.64	.93	.99	.82	1.01
Owyhee									
F	3	1.82	1.88	1.79	1.82	1.77	1.87	1.77	1.61
	8	1.82	1.86	1.82	1.72	1.73	1.73	1.65	1.74
Jory***506									
3.6	3		.22	.22			.17	.19	.22
	8		.14	.10			.15	.11	.28
Jory 508									
2.9	3		.30	.34	.32	.20	.29	.36	.24
	8		.19	.18	.22	.17	.19	.13	.14
2.2	3		.34	.48	.40	.34	.25	.28	.30
	8		.38	.38	.32	.28	.25	.26	.20
Jory 510									
6.6	3				1.56	1.47	1.60	1.98	1.82
	8				.60	.97	.97	.94	.77
6.1	3		.73	.86	.66	.81	.62	.60	.72
	8		.50	.58	.50	(.83)	.60	.40	.42

Table 2. (Continued)

Soil Series and Plots		Sampling Date						
		10/61	12/61	2/62	4/62	6/62	8/62	10/62
Laki		Millequivalents per 100 grams						
C	3	.90	1.08	.89	.81	.72	.82	.89
	8	.98	.93	1.01	.88	.83	.86	.89
F	3	3.78	3.54	3.48	3.16	3.54	3.96	4.10
	8	3.24	3.12	3.00	2.73	2.72	2.84	3.20
Walla Walla								
C	3	2.02	1.82	1.77	1.73	1.76	1.84	1.74
	8	1.99	1.89	1.77	1.70	1.76	1.74	1.68
F	3	1.79	1.79	1.67	1.66	1.66	1.68	1.65
	8	1.76	1.79	1.57	1.66	1.69	1.68	1.68

* C = cropped, F = fallow, 3 = 0" - 3", 8 = 3" - 8", () = inconsistent value, blank spaces = value not determined.

** This Astoria site has above average exchangeable K values for this series.

*** Numbers 3.6, 2.9, 2.2 etc. represent plots within each Jory site.

to expect different results in other years with normal rainfall patterns.

Provided the laboratory measurements are accurate, then increases or decreases in exchangeable cations must be due to corresponding changes in the amount of potassium on the complex. The most clearly demonstrated way in which decreases can occur is by fixation due to interlayer trapping as a result of high degrees of K saturation or drying. This reaction would tend to be reversed upon rewetting resulting in increases in exchangeable K. This reaction should be small in some illitic or kaolinitic soils, or in soils where changes in moisture were not sufficient to produce collapse of the lattice. Those soils which showed little or no seasonal changes (Dayton F, Woodburn F, Owyhee F, Jory 3.6 and Jory 2.9 which had a minimum of cropping, and Walla Walla F) appear to conform to this pattern. Most of the corresponding cropped plots (Dayton C, Jory 2.2, and Walla Walla C) showed a decrease as the growing season progressed, while the Woodburn C showed no change. (Similar seasonal information for cropped plots is presented in Table 1 of the Appendix, in which half of the soils showed a continual decrease from April to December.) The above soils which are high in illitic or kaolinite-like minerals under fallow conditions showed rather constant exchangeable K levels when sampled repeatedly over a period of months. Cropping these soils resulted in

observable reductions of the exchangeable K levels during a growing season. Why the Woodburn soil did not show this decline may be explained by its high potassium supplying power (14) and rather limited cropping during the experiment.

Those soils (Willamette, Quillayute and Astoria) containing a strong 14 \AA° component as their predominant clay mineral did not show trends which fit the above pattern and appear to have the greatest amount of variation between samples. These soils contain a number of types of clay minerals which may be affected by wetting and drying and also increase the complexity of the soil. The Willamette soil did not show distinct trends although the variation between samples was less than in the Quillayute and Astoria. It appears therefore that soils predominant in montmorillonite- and vermiculite-like clay minerals show variable exchangeable K levels when sampled repeatedly over a period of months. The Jory 510 probably also fits best into this class although its 14 \AA° component is more chloritic. This Jory site has also been shown by field experiments to be different from the other Jory sites with respect to potassium status and availability. ^{4/}

The two remaining soils (Deschutes and Laki) which were non-diffracting showed considerable variability under fallow

^{4/} Personal communication with T. L. Jackson, Oregon State University Soils Department.

conditions but less under cropped conditions. The accurate measurement of exchangeable K in these soils is expected to be more difficult than in soils containing a greater amount of crystalline minerals. The effect of cropping may be the same as that described later for the Jory soils, in which the variation between samples was reduced by the crop.

Changes in Exchangeable K and Ca upon Drying

Table 3 contains exchangeable K and Ca analyses for moist and oven dry samples from eight different soil series.

In the case of the Astoria, Deschutes, Willamette and Owyhee soil series the samples with the high moisture contents represent field moist soils. For each of these soils these are corresponding air-dried samples, as indicated by the same oven dry values. All other samples were air-dried prior to analysis. For each of the Jory soils three of the plots represent check plots while the other three are from the $L_2 P_2 K_0$ treatment. The differences between the two sets of plots is generally observed by their differences in calcium. The only two soils which showed consistent potassium decreases upon drying were the Willamette and the Jory 108. Also the Astoria showed occasional decreases upon drying. All the other soils showed increases upon drying in almost every instance. This change in

Table 3. Changes in Exchangeable K and Ca upon Drying.*

Soil Series and plots		% M	K _m	K _o	Ca _m	Ca _o	K _o -K _m	Ca _o -Ca _m
Astoria		Millequivalents per 100 grams						
C	3	3.6	1.50	1.70	3.7	5.0	+ .20	+1.3
	8	3.3	1.29	1.14	2.5	2.6	- .15	+ .1
	16	2.9	.73	.72	1.7	1.8	- .01	+ .1
F	3	3.7	2.29	2.06	4.1	4.0	- .23	- .1
	8	3.1	1.03	.98	2.0	2.3	- .05	+ .3
	16	3.0	.85	.86	1.0	0.8	+ .01	- .2
C	3	5.8	1.42	1.36	4.0	3.6	- .06	- .4
	8	5.5	.98	.92	2.0	1.9	- .06	- .1
	16	4.9	.65	.67	.9	1.0	- .02	- .1
F	3	5.9	1.30	1.30	3.2	2.8	.00	- .4
	8	5.9	.86	.87	1.4	1.4	+ .01	.0
	16	6.3	.54	.54	.7	0.6	.00	- .1
C	3	57.5	1.50	1.70	3.8	5.0	+ .20	+1.3
	8	50.0	1.50	1.14		2.6	- .36	
	16	39.6	.66	.72	1.8	1.8	+ .06	.0
F	3	60.1	2.06	2.06	4.6	4.0	.00	- .6
	8	50.3	.86	.98	1.5	2.3	+ .12	+ .8
	16	42.4	.97	.86	.9	0.8	- .11	.0
Deschutes								
C	3	.6	.94	.99	4.2	4.5	+ .05	+ .3
	8	1.0	.85	.92	4.5	5.0	+ .07	+ .5
	16	.9	.85	.86	4.5	4.8	+ .01	+ .3
F	3	.9	1.04	1.22	4.4	5.4	+ .18	+1.0
	8	1.3	.80	.98	4.3	5.0	+ .18	+ .7
	16	.9	.64	.72	3.8	4.0	+ .08	+ .2
C	3	1.5	1.10	1.18	3.8	3.8	+ .08	.0
	8	1.6	.67	.72	3.7	3.8	+ .05	+ .1
	16	1.8	.34	.45	3.2	3.5	+ .11	+ .3
F	3	1.7	.83	1.00	4.3	4.8	+ .17	+ .5
	8	1.7	.78	.84	4.2	5.2	+ .06	+1.0
	16	1.6	.78	.90	3.4	3.4	+ .12	.0
C	3	24.7	.90	.99	4.2	4.5	+ .09	+ .3
	8	18.4	.80	.92	4.5	5.0	+ .12	+ .5
	16	16.2	.85	.86	4.6	4.8	+ .01	+ .2
F	3	25.9	.93	1.22	4.9	5.4	+ .29	+ .5
	8	19.9	.79	.98	4.5	5.0	+ .19	+ .5
	16	16.6	.66	.72	4.0	4.0	+ .06	.0

Table 3. (Continued)

Soil Series and plots		% M	K _m	K _o	Ca _m	Ca _o	K _o -K _m	Ca _o -Ca _m
Millequivalents per 100 grams								
Dayton								
C	3	2.4	.54	.60	2.6	2.2	+.06	-.4
	8	2.3	.24	.34	4.9	4.6	+.10	+.3
	16	3.0	.26	.42	7.0	7.5	+.16	+.5
F	3	2.4	.60	.72	4.4	4.6	+.08	+.2
	8	2.4	.34	.44	5.4	5.6	+.10	+.2
	16	2.5	.30	.40	6.0	6.0	+.10	.0
Tillamook								
C	3	9.5	.72	.77	10.4	9.1	+.05	-1.3
	8	9.0	.50	.65	4.9	4.0	+.15	-.9
	16	8.9	.38	.52	4.0	2.8	+.14	-1.2
F	3	9.1	.56	.79	4.8	3.6	+.23	-1.2
	8	8.9	.48	.63	5.1	4.0	+.15	-1.1
	16	8.3	.44	.56	3.0	2.2	+.16	-1.2
Woodburn								
C	3	2.2	.70	.79	4.6	4.5	+.09	-.1
	8	2.3	.50	.65	5.1	5.2	+.15	+.1
	16	2.5	.56	.65	5.9	5.6	+.09	+.3
F	3	2.1	.58	.72	4.9	5.0	+.14	-.1
	8	2.2	.51	.65	5.3	5.4	+.12	-.1
	16	2.3	.51	.65	5.3	5.4	+.14	+.1
Willamette								
C	3	2.3	1.00	.78	5.7	7.7	-.22	+2.0
	8	2.3	.74	.70	5.8	6.0	-.04	+.2
	16	2.1	.90	.76	5.1	5.8	-.14	+.7
F	3	2.3	1.02	.77	4.8	5.2	-.25	+.4
	8	2.1	.90	.89	5.0	5.0	-.01	.0
	16	2.0	.70	.64	4.8	5.1	-.06	+.3
C	3	31.4	1.16	.78	5.9	7.7	-.38	+1.8
	8	29.7	.74	.70	5.8	6.0	-.04	+.2
	16	29.7	.74	.76	5.7	5.8	+.02	+.1
F	3	31.7	1.00	.77	5.3	5.2	-.23	-.1
	8	28.3	1.04	.89	4.9	5.0	-.15	+.1
	16	22.5	.70	.64	5.3	5.1	-.06	+.2
Owyhee								
F	3	2.4	1.90	2.14	11.3	12.2	+.24	+.9
	8	2.8	1.88	2.05	11.6	12.2	+.17	+.6
	16	2.8	1.36	1.50	12.4	13.0	+.26	+.6
F	3	33.4	1.84	2.14	12.1	12.2	+.30	+.1
	8	22.4	1.84	2.05	12.0	12.2	+.19	+.2
	16	21.3	1.19	1.50	12.6	13.0	+.31	+.4

Table 3. (Continued)

Soil Series and plots	% M	K _m	K _o	Ca _m	Ca _o	K _o -K _m	Ca _o -Ca _m
Millequivalents per 100 grams							
Jory 108							
2.4	3.6	.26	.22	7.3	7.2	-.04	- .1
2.8	3.8	.50	.45	9.6	10.5	-.05	+ .9
4.6	3.6	.37	.36	11.0	11.0	-.01	.0
6.9	3.6	.24	.22	7.6	7.8	-.02	+ .2
8.3	3.7	.20	.18	10.7	11.0	-.02	+ .3
8.6	3.8	.34	.28	7.0	6.7	-.06	- .3
Jory 506							
1.5	4.2	.17	.09	11.0	9.9	-.08	-1.1
3.6	4.1	.11	.13	7.7	7.1	+.02	- .6
5.1	4.4	.14	.13	7.6	7.2	-.01	- .4
5.5	4.4	.14	.13	12.8	13.4	.01	+ .6
7.4	4.1	.14	.14	12.5	12.7	.00	+ .2
8.7	4.3	.12	.13	8.7	5.9	+.01	-2.8
Jory 508							
2.2	4.0	.32	.31	11.9	12.0	-.01	+ .1
2.9	4.1	.52	.56	12.5	12.2	+.04	- .3
3.7	4.0	.30	.31	3.7	3.3	+.01	- .4
4.11	4.0	.25	.26	6.3	6.2	+.01	- .1
5.1	3.9	.16	.21	3.8	3.3	+.05	- .5
6.12	4.1	.34	.40	3.2	2.3	+.06	- .9
Jory 510							
2.2	4.2	.54	.63	14.1	13.7	+.09	- .4
3.1	3.3	.70	.84	9.6	9.6	+.14	.0
4.2	3.1	.51	.60	12.8	13.4	+.09	+ .6
6.1	3.4	.48	.61	9.0	8.6	+.13	- .4
7.6	3.2	.60	.76	11.3	11.2	+.16	- .1
8.3	3.3	.44	.52	8.8	8.5	+.08	- .3
Jory 514							
2.4	3.9	.52	.56	14.0	13.4	+.04	- .6
2.8	3.9	.36	.40	6.5	6.1	+.04	- .4
4.6	3.8	.22	.26	6.8	6.5	+.04	- .3
6.9	3.9	.65	.68	10.6	10.2	+.03	- .4
8.3	4.0	.30	.34	10.0	7.0	+.04	-3.0
8.6	3.8	.65	.76	15.0	16.8	+.11	+1.8

* C = cropped, F = fallow, 3 = 0"-3", 8 = 3"-8", 16 = 8"-16", K_m = K moist, K_o = K oven dry, Ca_m = Ca moist, Ca_o = Ca oven dry, %M = percent moisture content. Depth of Jory samples was 0" - 8".

exchangeable K appeared to be greater between air- and oven-dried samples than between field moist and air-dried samples. The amount of exchangeable K decreased with depth in almost every instance where three depths were taken. This could be attributed to a decrease in organic matter.

Routine measurements of exchangeable K are subject to negative errors, that is, an underestimation of the total amount of exchangeable K which may be obtained by longer shaking or by wetting, as will be discussed later. One normally states that fixation has occurred whenever a dry K value is observed which is below the corresponding moist K value. Any measurement which is below the moist value correctly defines fixation, provided the dry determination is not an underestimation. If the latter is the case, then we have erroneously defined the difference between the two measurements as fixation or we may have overestimated the magnitude of the difference. A similar argument can be stated with regard to potassium release which shows the accuracy of the measurement of the moist soil can be a determining factor. Since there is reason to doubt the accuracy of both these determinations it is very difficult to state that fixation or release has absolutely occurred in any of the soils studied.

The increase and decrease of calcium upon drying are presented as partial demonstration that there may be error at one or both of the moisture levels in the equilibration procedure for measuring exchangeable cations since no differences would be expected to occur for calcium with drying. The lattice entrapment mechanism which is used to explain large changes in potassium would not generally be expected to apply to calcium. Even if such a mechanism did affect calcium the direction of the change would be expected to be the same as for potassium. However the two cations did not always change in the same direction so there does not appear to be a definite connection between potassium and calcium through some such mechanism.

The Effect of Cropping on Exchangeable K in the Jory Soil

Soils from eight of the nine Jory sites given in Table 4 gave measurable decreases in air dry exchangeable K after three to four years of cropping with alfalfa, as can be seen by comparing the original and treated columns. Only site 108 showed an increase with time. Unfortunately, X-ray data were not obtained for this site. However, it is of interest that this Jory soil appeared to be somewhat different from the other Jory sites as reported in the previous

Table 4. Effect of Cropping on Exchangeable K in Soils from Nine Jory Sites, 0" - 8" Depth. *

Site No.	Exchangeable K		
	Original [†]	Check Plots	Treated Plots
	Millequivalents per 100 grams		
108	.26	.28	.35
502	.54	.64	.30
506	.51	.12	.15
508	.50	.39	.24
510	.74	.54	.55
512	.89	.75	.66
514	.50	.61	.29
516	.47	.25	.23
518	.23	.18	.17

* Cropping was with alfalfa for three or four years depending on the site. The check plots ($L_0 P_0 K_0$) within a replication had the least amount of crop during this period. The check plots of 514 were changed to $L_2 P_2 K_2$ in 1961. The treated plots ($L_2 P_2 K_0$) received the same treatments at all sites.

[†] Taken from Table 16. Annual Report for 1960 Project Agreement No. Oregon 863.2 obtained from Dr. T. L. Jackson, Oregon State University Soils Department.

section. The check plots of the eight sites mentioned above generally showed some decrease, when compared with the original values given for these plots. (Table 2 of the Appendix contains the individual values from each replication for both the check and treated plots from which the statistical data was calculated.)

The original values given in the table were obtained by averaging the three composite samples taken from each of the three replications. The check plot values were obtained three or four years later by averaging the three check plots. If the soil is sufficiently variable within each replication there is no reason to expect any one check plot to have the average value for that replication, and there is less probability that all three of the check plots will have values which are nearly equal to the average values of their respective replications. For example site 502 has the three values of .96, .65 and .31 for its three check plots.

In the case of the treated plots, which were higher yielding than check plots, all three of the individual values which comprise the average fall below the corresponding original composite value except for site 108. Also the three values from the treated plots are more closely clustered than the corresponding check plot values. For example, site 502 has .37, .31 and .28 as its three treated plot values.

This difference due to amount of cropping is substantiated by calculating the pooled sample variance (S_p^2) for the check plots as a whole and the more heavily cropped plots as a whole. If this is done, excluding the Jory 108 site due to the irregularities mentioned above, the pooled variance for the checks is $3690/16 = 230.6$ with 16 d. f. and the pooled variance for the treated plots is $698/15 = 46.5$ with 15 d. f. Therefore F is $230.6/46.5 = 4.96^*$ with 16 and 15 d. f. and the variances are significantly different at the five percent level. The inference is therefore that cropping may have reduced the original population variance by removing more K from plots high in K than those originally low in K. With this reduced variance three plots can more accurately evaluate the exchangeable K level over the whole experiment than if the variance were higher. Since the population variance has changed less on the check plots, then nothing short of another composite sampling, which is impossible once the experiment is laid out, would be expected to give the same value as originally measured. Here the problem of soil heterogeneity seems to be of some importance.

The Effect of Shaking Time on Exchangeable K

Table 5 shows clearly that increased shaking time increased the amount of exchangeable K as measured by equilibration. It would be expected that for both air dry and oven dry samples this slow equilibrium is due to slow wetting of the fine soil pores filled with air. Soils high in organic matter and pore space will probably exhibit this effect the most.

Table 5. Effect of Shaking Time on Exchangeable K in Air Dry Samples

Soil Series	Depth Ins.	Shaking Time		Increase
		30 min.	24 hr.	
Millequivalents per 100 grams				
Deschutes	3-8	.675	.720	.055
Woodburn	3-8	.625	.701	.055
Quillayute	3-8	.545	.634	.109
Dayton	3-8	.240	.304	.056
Dayton	0-5	.262	.376	.114
Dayton	0-5	.255	.351	.096

The moist Dayton soils also showed an increase in exchangeable K as the shaking time was increased, as shown in Figure 2, and this obviously was not due to slow rewetting. The amount of increase which could be obtained over a 24 hour period depended not only upon the soil sample being tested but also on the moisture content of the sample. The magnitude of this increase for the two moist surface soils was not quite as much as that observed in the air and oven dried samples, although there was no reason to expect that the two rates of exchange would be the same or in fact that the upper limits would always be exactly equal. A soil that has been dried and rewetted by the exchanging solution is apparently a somewhat different system than one in which the internal moisture does not initially contain a high concentration of the exchanging cation. It is expected that soils high in organic matter, clay, and water stable aggregates will show this effect the most. Whatever the mechanism or

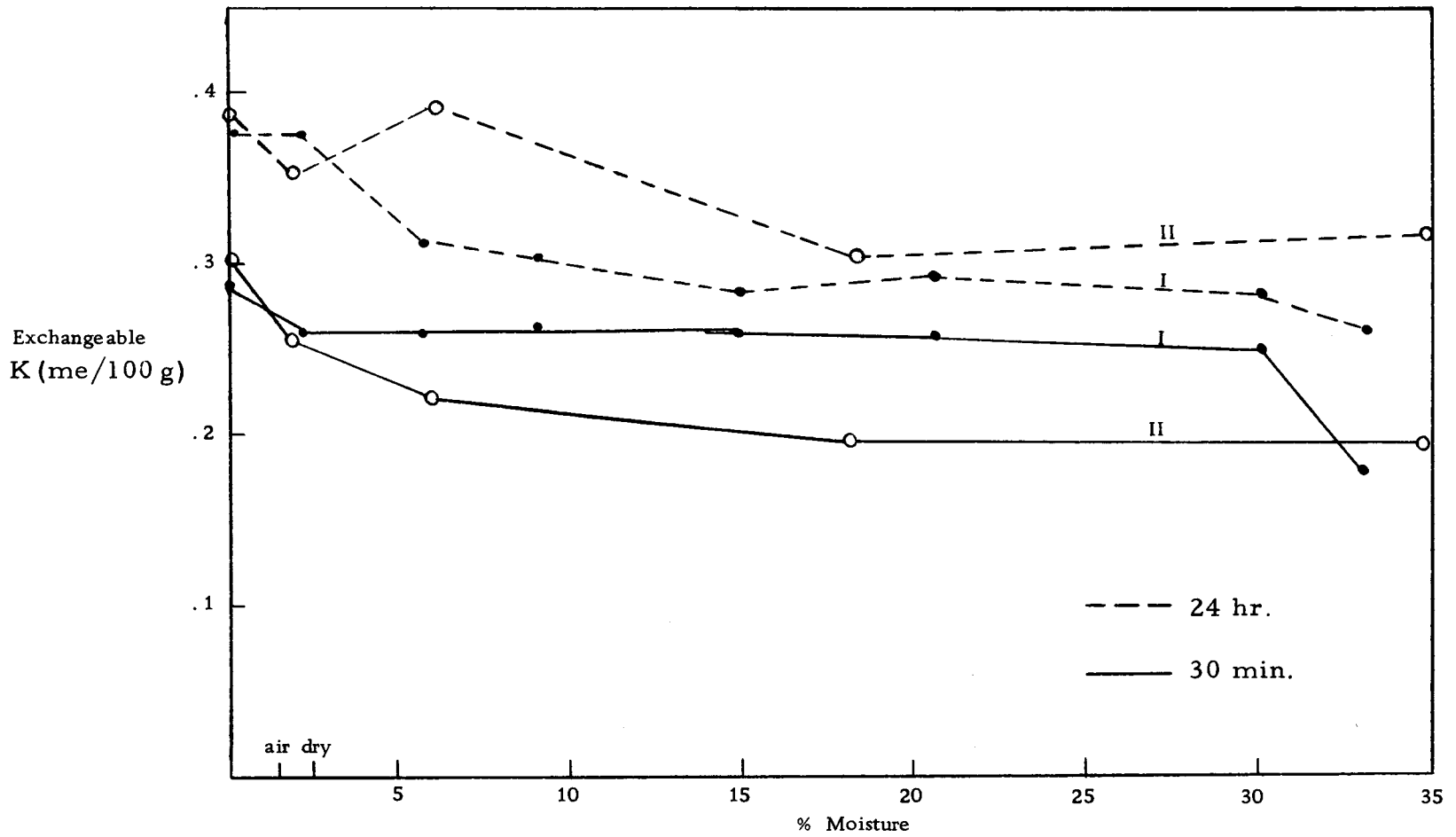


Figure 2. The Effect of Shaking Time on Exchangeable K with Decreasing Moisture Contents of Two Dayton Surface Soils (I and II).

mechanisms involved at different moisture levels it does not seem justifiable to attribute the differences between the dry and moist samples at short equilibrium times, and possibly longer ones also, to potassium release from the clay mineral structure itself.

Also the two similar Dayton soils in Figure 2 more closely approached each other at moisture contents below five percent regardless of the shaking time. Although no moisture level estimates the total amount of exchangeable K which can be exchanged better than any other one, there appears to be more in favor of the dried (less than five percent moisture) analysis than the moist for this particular soil.

The Effects of Wetting and Heating Upon Exchangeable K

Table 6 contains some data for two Dayton surface soils which demonstrates two factors which may be related to the determination of exchangeable cations in the same manner as shaking time. If wetting is a limiting factor in dried soil then it would be expected that a wetting agent would speed up the rate of wetting and therefore give higher exchangeable K values at any particular shaking time. This effect was in fact demonstrated for an oven dry sample by as much as a 30 percent increase over a 24 hour period. No attempt was made to measure the time required to completely wet a sample which

Table 6. Effect of Wetting and Heating on Exchangeable K of Two Dayton Surface Soils.

Soils	< 20 μ fraction	Organic Matter	Moisture	Exchangeable K				
				no wetting agent		wetting agent		80°C
				30 min.	24 hrs.	30 min.	24 hrs.	30 min.
		Percent		Millequivalents per 100 grams				
I	76.8	2.26	0.0	.289	.378	.352	.442	
	"	"	2.1	.262	.376	.334	.433	.356
	"	"	33.0	.180	.288			.346
II	76.6	1.70	0.0	.304	.328	.400	.428	
	"	"	1.8	.255	.300	.366	.386	.346
	"	"	36.0	.193	.319			.322

would no doubt vary considerably from soil to soil. The process of wetting may be of two or more types. One may be related to slow vapor diffusion into air pockets which develop in dead-end pores or between particle surfaces when wetting occurs from two sides at once. Another may be related to slow hydration of the hydrophobic components of the soil, especially if they have absorbed cations on their surface which are not highly hydrated.

The reaction which slows equilibrium in the moist soil is not fully clear. Increasing the thermal energy of the extractant by heating it to 80 - 90°C prior to equilibration gave a marked increase in exchangeable K on the moist soil. The increase for dry soils was possibly related to wetting through a change in vapor

pressure, but the increase produced in the moist samples was not investigated fully enough to allow an explanation. These results indicate that there may be differences between moist and dried samples which are not basically related to fixation and release mechanisms from within the crystal lattice but may be more a function of the physical properties of the colloidal particles with which the cation exchange must occur. Therefore it would be expected that soils which are physically different would not react similarly when analyzed by chemical procedures which require the movement of bulk solution within the soil's fine pore space.

SUMMARY AND CONCLUSIONS

The main question that this research project set out to answer was whether or not there is a cyclic increase and decrease in exchangeable potassium due to seasonal changes in soil moisture. Is the exchangeable potassium measured during a wet season a reliable evaluation of potassium for the summer months when the soil is drier? The conclusion of this thesis is that the wetting and drying observed in the field do not result in consistent seasonal variations on any of the soils studied. This does not mean that there may not be a seasonal fluctuation in exchangeable potassium due to some other factor such as cropping; or that consecutive sampling of a variable soil will always give the same results. Both of these factors must be considered in evaluating a soil test result and making a corresponding fertilizer recommendation, especially where field soil test values and yield responses are correlated.

On the other hand, controlled moisture conditions do produce differences in exchangeable potassium measured by the same procedures in the laboratory. Similar changes can be produced by altering the physical nature of the extraction procedure through increased shaking time, a decreased surface tension of the extracting solution or an increased temperature of the extracting solution.

Exchangeable calcium is not the same at different moisture levels. Therefore it does not seem likely that the drying effect in the laboratory is related to changes in potassium availability to plants by a shift in the potassium equilibrium (fixation and release) of the soils studied, but rather is related to the physical aspects of the exchange procedure itself. This interpretation is somewhat different than generally described in the literature. From this point of view an air dry analysis appears to give a more useful evaluation of exchangeable potassium in the soils studied than does a moist analysis, although neither method gives a complete estimate of the amount of cation that can be exchanged.

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APPENDIX

APPENDIX

Table 1. Seasonal variations in air dry exchangeable K on cropped plots, 0" - 8" depth.

Series and Plots	Dates of Sampling				
	4/62	6/62	8/62	10/62	12/62
	Millequivalents per 100 grams				
Ch 1	.50	.54	.54	.46	.43
Ch 2	1.72	1.22	1.10	1.08	1.04
Ch 3	.99	.82	.83	.70	.68
Da 1	.24	.19	.27	.30	.23
Da 2	.37	.30	.24	.30	.22
Jo 1	.20	.28	.16	.14	.26
Jo 2	.56	.38	.23	.33	.36
Jo 3	.26	.18	.23	.22	.18
Jo 4	.35	.30	.25	.27	.24
Jo 5	1.17	1.17	1.21	1.33	1.17
Jo 6	.56	---	.61	.48	.53
Me 1	.64	.62	.57	.60	.50
Me 2	.84	---	.88	.76	.70
Me 3*	.40	---	.46	.45	.49
Po 1	.40	.20	.12	.32	.25
Po 2	.15	.11	.21	.14	.22
Po 3	.86	.56	(.90)	.63	.58
Si 1	.40	.44	.48	(.65)	.43
Si 2	1.26	1.07	1.24	1.31	1.30
Si 3	.64	---	.90	1.12	.67
Wi 1	.86	.98	1.01	1.20	.95
Wi 2	.46	.51	.37	.48	.63

* fallow plot

Ch = Chehalis, Da = Dayton, Jo = Jory, Me = Melbourne, Po = Powell, Si = Sifton, Wi = Willamette () = inconsistent values

Table 2. Exchangeable K values from Jory sites 0" - 8" depth.

Site	Rep.	Check plots*			Treated plots †		
		I	II	III	I	II	III
Millequivalents per 100 grams							
502		.96	.65	.31	.37	.28	.25
506		.11	.14	.12	.17	.14	.14
508		.52	.30	.34	.32	.25	.16
510		.70	.48	.44	.54	.55	.60
512		.59	.74	.94	.52	.72	.74
514		.52	.65	.65	.36	.22	.30
516		.23	.18	.34	.21	---	.25
518		.18	.13	.22	.13	.14	.23

* Check plots represent $L_0 P_0 K_0$ plots. Site 514 was changed to $L_2 P_2 K_2$ in 1961.

† Treated plots represent $L_2 P_2 K_0$ plots.