

SORPTION OF POTASSIUM AND AMMONIUM BY SOILS  
AS INFLUENCED BY CONCENTRATION AND  
THE DEGREE OF BASE SATURATION

A THESIS SUBMITTED TO THE GRADUATE DIVISION OF THE  
UNIVERSITY OF HAWAII IN PARTIAL FULFILLMENT  
OF THE REQUIREMENTS FOR THE DEGREE OF  
MASTER OF SCIENCE

JUNE 1941

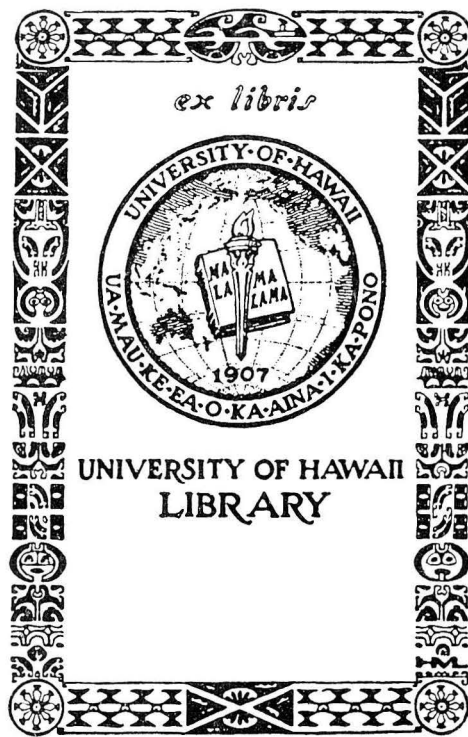
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Many of the agricultural soils in high rainfall regions of the Hawaiian Islands are in a low state of base saturation. Because of the high rainfall which, in the most humid districts, is above 200 inches annually, knowledge of the abilities of these soils to retain potassium and ammonium fertilizers becomes important to the sugar cane grower. It has been shown by Peech and Bradfield (6) and more recently by Peech

(7) that the abilities of soils to sorb potassium from neutral potassium salts decrease as the degree of base saturation decreases. It seems probable that sorption of ammonium is similarly affected by the state of saturation. In view of these considerations it was deemed appropriate to study the effect of the degree of base saturation of these soils upon their abilities to sorb potassium and ammonium salts.

It is a common practice in Hawaii to apply nitrogen and, at times, potassium to sugar cane by dissolving the fertilizer in the irrigation water prior to its application to the field. Since an irrigation of sugar cane involves from 5 to 10 acre-inches of water, the resulting dilution of the salt is great. The effect of such dilution upon the sorption of the salts by Hawaiian soils has not previously been studied. A second objective of this work, therefore, was to determine the influence of concentration upon the sorbability of potassium and ammonium by the soil.

Experimental Procedure

Two soils were selected for the study: one, a Hilo-coast soil from the Island of Hawaii, is representative of soils of the more humid districts

where irrigation is unnecessary; the other, from the Aiea region of the Island of Oahu, is typical of large areas of drier, irrigated sugar cane lands of the Islands. Both soils are residual and lateritic in nature. Certain other characteristics of these soils are listed in Table 1.

Substantial quantities of the two soils were pulverized to pass a 1-mm. screen. They were then saturated with calcium by leaching with a solution (pH 6.8) which was 0.5 N with respect to calcium acetate and 0.1 N with respect to calcium chloride. The chloride was included to simplify the testing of the washed soil. After treatment with the calcium solution, the soils were washed with water until free of chlorides. As a result of this treatment the pH of each soil was 7.4. One hundred-gram portions of these calcium-saturated soils were then adjusted to various degrees of saturation by electrodialysis. In the case of the Hilo-coast sample, soils at eight stages of base saturation were prepared in this manner; with the Aiea soil, three. Since ammonium is applied almost exclusively by the plantations as the sulfate in fertilization and potassium as the chloride, these salts of the cations were employed in the study.

The abilities of the two soils at the various degrees of calcium saturation to sorb potassium and ammonium were measured by the following procedure: Duplicate 5-gm. samples of the air-dried prepared soils were shaken with 250 cc. of potassium chloride (or with ammonium sulfate) in an end-over-end shaker for 1 hour. The suspensions were allowed to stand 16 to 18 hours. They were then poured on filters in 8-cm. Buchner funnels and the solutions drawn through under suction. Additional units of 500 cc. of the fresh solutions were then percolated through the soils under gravity,

the rate of percolation being so adjusted that the process required 16 to 20 hours. Upon completion of the percolation, the soils were washed with 80 per cent ethyl alcohol until free of soluble salt. Where potassium was the sorbed cation, the amount was determined by subsequent displacement with a normal ammonium acetate solution adjusted to pH 6.8. The potassium thus displaced was determined by the volumetric sodium cobaltinitrite method of Volk and Truog (9). The sorbed ammonium was determined by distillation with magnesium oxide, corrections being made for any breakdown of organic soil nitrogen in the process by similarly distilling samples of the untreated completely electrodyalized soils. In order to ascertain the effect of concentration upon the sorption of potassium and ammonium by the soil, three solutions of each salt were employed; namely, 0.001, 0.01 and 0.1 N.

It was manifestly impossible to vary the concentrations of the salts and at the same time to maintain constant both the ratio of salt to soil and that of soil to solution. It was therefore decided to employ a constant ratio of soil to solution and to ignore the factor of the unequal ratios of salt to soil. This appears to have been justified, since the amounts of the cations sorbed by the soils were not sufficient to decrease more than slightly the concentrations of the solutions, except in the case of the highest dilution, 0.001 N. Even here the maximum decrease was less than 10 per cent. Moreover, this represents an average decrease, whereas the actual decrease was probably greater than this value at the beginning of the percolation and very much less at the end.

#### Sorption of Potassium

Fixation of potassium in nonreplaceable forms has been shown by

Volk (8) and Lyman (5) to occur to only a slight extent in Hawaiian soils and then only as a result of repeatedly wetting and drying the soils. Hence, it is assumed that fixation of potassium in such forms did not occur under the conditions of this experiment and that all the potassium sorbed under the various treatments was subsequently replaced by ammonium acetate.

The results obtained for the sorption of potassium at various degrees of calcium saturation by the Hilo-coast soil are shown in Fig. 1. They indicate that increasing the amounts of exchangeable calcium in this soil increases its ability to sorb potassium. The degree to which exchangeable calcium is effective in increasing the sorption of potassium by the soil is seen, however, to be dependent upon the concentration of potassium in the solution with which the soil is leached. Thus, whereas saturating the completely electro dialyzed soil with calcium approximately doubled the quantity of potassium sorbed from the 0.001 N KCl solution, it increased by a factor of five the amount sorbed from the 0.1 N solution. The slopes of the curves in the figure indicate that the beneficial effect upon the sorption of potassium of increasing amounts of exchangeable calcium is greater at the lower degrees of base saturation. This suggests that liming would prove most effective upon those soils which are most nearly devoid of exchangeable bases.

Table 2 shows results for the sorption of potassium by the Aiea soil at three stages of saturation, together with corresponding data for the Hilo-coast soil. It will be seen from this presentation that augmenting the supply of exchangeable calcium in the Aiea soil resulted, as in the

case of the Hilo-coast soil, in increased sorption of potassium. In fact, the quantities of the salt sorbed by these two very diverse types of soil are, except at the highest concentration of potassium chloride, of much the same order. With the highest concentration, and at the higher degrees of calcium saturation, sorption by the Hilo-coast soil was much greater. The difference in sorption power at this point is probably conditioned in part by the very unequal exchange capacities of the two soils. Thus the amount of potassium taken up from 0.1 N KCl by the saturated Hilo-coast soil (17.5) is the equivalent of the entire exchange capacity of the Aiea soil. In every case the degree of potassium saturation resulting from the various treatments was greater for the Aiea soil.

Since potassium (from potassium chloride) apparently replaces exchangeable calcium in the soil more readily than it does exchangeable hydrogen, there seems little doubt but that increasing the degree of base saturation in the more highly leached soils of the high rainfall districts would aid substantially in bringing about a greater sorption of potassium. There is a vast difference, however, between raising the level of exchangeable calcium throughout the root zone and the mere application of lime to the soil. Brown and Munsell (1) found that, after application of lime to grassland soils, a period of 10 years was required before a uniform pH was attained in the top 6 inches of soil. The problem of obtaining the necessary distribution of lime in the root zone of sugar cane would be especially difficult under Hawaiian conditions where the fields are plowed and planted only at intervals of 5 to 10 years. Hence, it appears that, though ultimately the use of lime would prove beneficial in retarding possible losses of potassium in the high rainfall regions of the Islands,

little immediate gain could be expected from its use.

Fig. 1 and Table 2 show that the effect of the concentration of the potassium solution upon sorption of this cation by the soil is just as important as that of the degree of base saturation, if not more so. From 0.001 N KCl the quantities of the cation taken up were only one-fourth to one-twelfth the amounts sorbed at the same degrees of saturation from 0.1 N KCl. The marked decreases in the sorption of potassium with decreasing concentrations of potassium chloride, together with the relatively slight sorption of the cation from the lowest concentration (in the neighborhood of 1 m.e. for both soils, at all degrees of saturation), suggest the possibility of a concentration so low that no sorption whatever by the soil would occur, regardless of the degree of base saturation. Hance and co-workers (3), studying the effect upon certain Hawaiian soils of irrigation water with naturally occurring potassium to the extent of 25 p.p.m.  $K_2O$ , concluded that sorption of potassium from this medium by the soil does not occur even when several hundred pounds of  $K_2O$  are applied annually.\* Expressed on the basis of normality, this concentration of potassium corresponds to approximately 0.0005 N, or but one-half of the minimum concentration of potassium chloride employed in the present study, which resulted in a maximum sorption of only 1.4 m.e. of potassium per 100 gms. of soil. There seems good reason to believe, therefore, that the failure of potassium-containing irrigation water to increase the level of exchangeable potassium in Hawaiian soils is due in very large part to the low concentration of the cation. Kelly, Brown and Liebig, Jr. (4)

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\*It was shown, however, that the crop was able to obtain potassium directly from the irrigation water.



and Fraps and Fudge (2) have shown that the degree to which sodium is sorbed by soils from irrigation water is dependent to a great extent upon the concentration of the cation in the medium. Their work indicates that it is due to the high dilution of the sodium in irrigation water that the base does not normally accumulate in the soil in injurious amounts. The same workers have also shown that other cations in the irrigation water, especially calcium, influence the sorption of monovalent bases.

The repressing effect of dilution upon the sorption of potassium by the soil suggests that the application of potassium fertilizers to crops through the medium of the irrigation water may result in losses of the nutrient. The extent to which such losses of potassium might be expected to occur would depend in part upon the quantity applied and the volume of irrigation water in which the salt is dissolved. Where potassium salts are applied to the soil in crystalline forms and brought into solution through subsequent rainfall, the concentrations of the salt and hence the associated sorption of potassium would be expected to range from very high to probably negligible values.

#### Sorption of Ammonium

Data relative to sorption of ammonium (from ammonium sulfate) by the two soils at three stages of base saturation are also shown in Table 2. Sorption of ammonium by both soils increased, as did that of potassium, with increasing degrees of calcium saturation, the effect being more pronounced on the Milo-coast soil. Sorption of ammonium by the two soils was similar in amount except at the highest concentration of ammonium sulfate, 0.1 N. Here the effect of exchange capacity upon the sorption of

ammonium is seen. Thus with the half and the completely calcium-saturated soils, sorption by the Hilo-coast soil considerably exceeded the entire exchange capacity of the Aiea soil.

Though the presence in the soil of exchangeable bases is thus seen to have a beneficial effect upon the retention of ammonium, yet a far more important factor appears to be the concentration at which the ammonium salt percolates through the soil. For example, on the Aiea soil, the quantities of ammonium sorbed from 0.1  $N$   $(NH_4)_2SO_4$  were from 8 to 10 times the amounts taken up from 0.001  $N$   $(NH_4)_2SO_4$ , whereas the maximum increases in sorption by this soil, due to base saturation, were less than twofold. The influence of concentration upon the sorption of ammonium by the Hilo-coast soil was still greater.

The results of this study suggest that when ammonium salts are applied to the soil through the medium of the irrigation water, the resulting state of sorbability of the ammonium ions is probably very low, depending upon the amount of fertilizer applied, the volume and quality of the irrigation water and the nature of the soil. The more dilute is the solution, the greater will be the tendency for the ammonium to go where the water goes. If the water containing the salt does not penetrate the soil to depths exceeding that of the root zone, it perhaps makes little difference whether the cations are actually sorbed by the soil or not; however, an irrigation of 7 acre-inches, which is normal under Hawaiian conditions, does in many soils reach depths considerably greater than those attained by important fractions of the sugar cane roots. Moreover, in the generally pervious soils of Hawaii, percolation of water is a

fairly rapid process. Under such circumstances, it seems probable that some ammonium may be lost.

Effect of the Anion on the Sorption of  
Potassium and Ammonium

The results of this study showed that, at the higher concentrations of the salts, the amounts of ammonium sorbed were much greater than the corresponding quantities of potassium sorbed, particularly by the Hilo-coast soil. The question naturally arose, therefore, whether the greater sorption of ammonium at these concentrations indicated a higher sorbability of ammonium, per se, or whether the difference in sorption of the two cations was attributable to the different natures of the accompanying anions. It was suggested that, since sulfuric acid is weaker than hydrochloric acid, more ammonium than potassium was sorbed by the soils because of the union of the sulfate radical with exchangeable hydrogen to form the bisulfate radical, thereby promoting the replacement of hydrogen by ammonium.\* If the respective anions were responsible for the differential sorption, then, if the soil were leached with potassium sulfate and ammonium chloride instead of with potassium chloride and ammonium sulfate, the sorption of potassium should exceed that of ammonium.\*\* In order to test this hypothesis, portions of the completely unsaturated Hilo-coast soil were leached with solutions of potassium sulfate and ammonium chloride in the manner already described, and the extent of the resulting sorption was determined.

It will be seen from Table 3 that interchanging the anions reversed

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\*The dissociation constant for the second hydrogen of  $\text{H}_2\text{SO}_4 = 2 \times 10^{-2}$ .

\*\*On this basis it is probable that substantial differences in the sorption of the cations from the two salts would result only where the sorption was brought about by percolation.

the order of the sorption of ammonium and potassium: under these conditions, much more potassium than ammonium was taken up by the soil at all concentrations. Thus there remains no evidence that one of the two cations is more strongly sorbed than the other, when both are employed as salts of the same acid. If the proffered explanation for the observed differences in sorbability of the cations from the chloride and sulfate forms is correct, it would be expected that such differences would be greatest on the hydrogen-saturated soils and would decrease as the proportions of exchangeable hydrogen to base in the soil exchange material decreased. Such relationships appear to be implied by the data in Table 2. Except at the lowest concentrations, the ratios of ammonium sorbed (from ammonium sulfate) to potassium sorbed (from potassium chloride) generally decreased with increasing degrees of base saturation. Though the evidence resulting from this test is definitely limited, the indications are that, on highly acid soils at least, greater sorption of potassium and ammonium may be expected to result from the use of sulfates than from the use of the corresponding chlorides.

#### Summary

A study was made of the sorption of potassium and ammonium from 0.1, 0.01 and 0.001 N solutions of the cations by two Hawaiian clay soils at degrees of calcium saturation ranging from 0 to 100 per cent. The results may be summarized as follows:

Sorption of potassium and ammonium (from percolating solutions) decreased greatly with decreases in concentrations of the cations. At the lowest concentration (0.001 N) the sorption was very low, ranging from 0 to 1.4 m.e. per 100 gm. of soil, depending upon the salt used and the degree of calcium saturation.

Increasing the degree of calcium saturation of the soils increased the sorption of potassium and ammonium. The effect was not so marked, however, as was that of the concentration.

Sorption of potassium and ammonium (by the completely electro-dialyzed soil) was much higher from the sulfates than from the chlorides of these cations.

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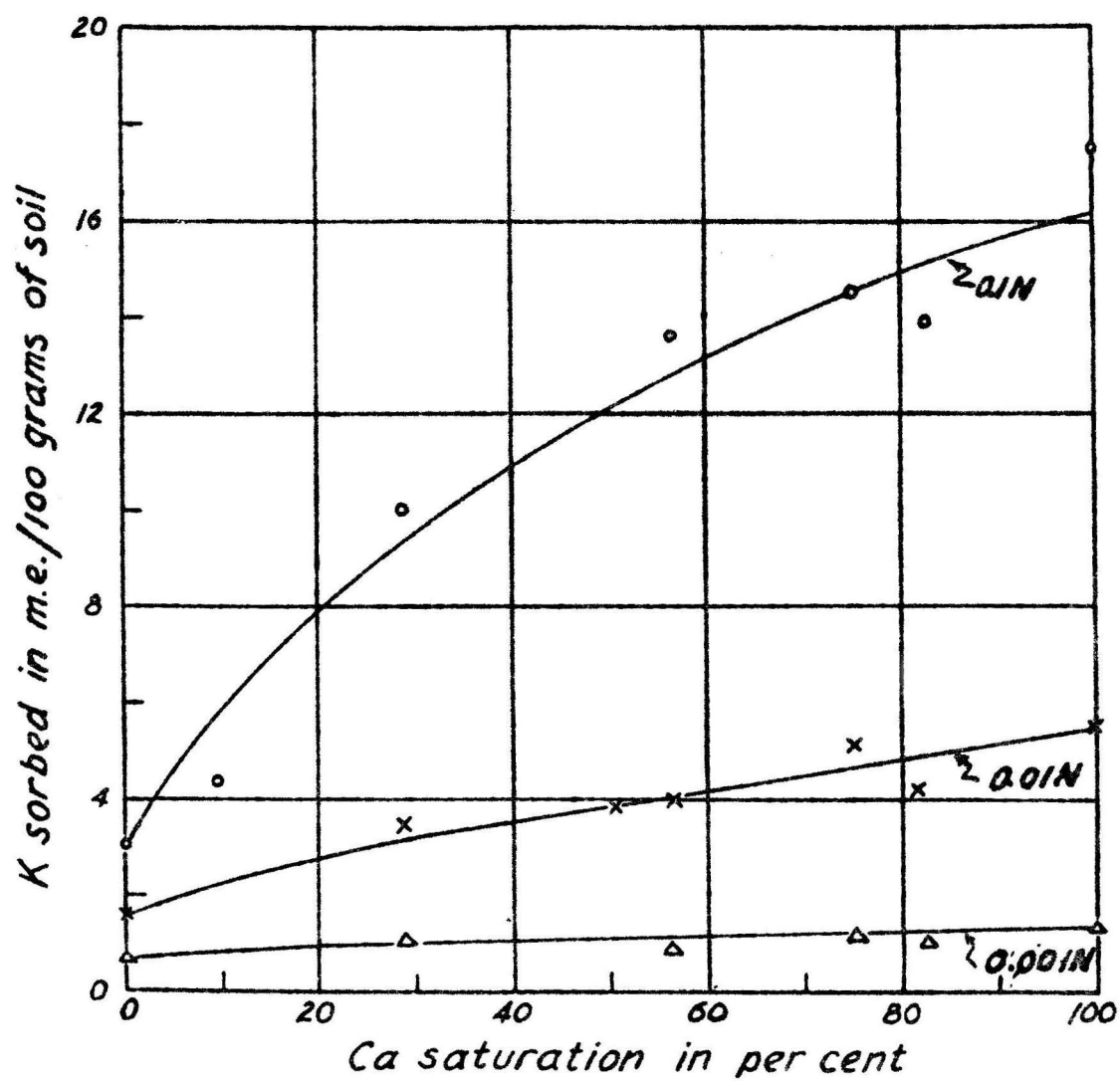


Figure: Potassium (from KCl) by the Hilo-coast soil as influenced by concentration and by the degree of saturation.

Table 1. Description and Some Chemical Characteristics of the Soils Studied

Soil	Description	Organic matter Per cent	Ultimate pH	Exchange capacity m.e./100 gm.	Exchange capacity due to organic matter Per cent
Hilo-coast	Light brown clay	15.6	4.3	41.2	76.6
Alea	Red clay	4.7	4.3	17.4	27.0

pH (Ca-soil) = 7.4

Table 2. Effect of the Concentration of the Percolating Solution and of the Degree of Base Saturation Upon Sorption of Potassium and Ammonium

Percolating solution	Degree of Ca-saturation					
	Hilo-coast soil			Alea soil		
	0	51	100	0	51	100
<u>Potassium sorbed, in m.e./100 gm. of soil</u>						
0.001 N KCl	0.7	1.1*	1.4	0.9	---	1.2
0.01 N KCl	1.6	3.9	5.5	1.9	4.4	4.4
0.1 N KCl	3.0	12.6*	17.5	4.2	5.9	7.9
<u>Ammonium sorbed, in m.e./100 gm. of soil</u>						
0.001 N (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	0.2	0.4	0.6	1.0	1.1	1.2
0.01 N (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	3.1	6.9	7.1	3.9	5.8	6.1
0.1 N (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	10.4	22.6	24.1	7.3	10.5	10.4

\*Obtained by interpolation from Fig. 1.



Table 3. Influence of the Anion on the Sorption  
of Ammonium and Potassium by the H-saturated Hilo-coast Soil

(Results expressed in m.e./100 gm. of soil).

Concentration of salt	Potassium sorbed from		Ammonium sorbed from	
	KCl	K <sub>2</sub> SO <sub>4</sub>	NH <sub>4</sub> Cl	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>
0.001 <u>N</u>	0.7	1.2	0.0	0.2
0.01 <u>N</u>	1.6	3.4	0.8	3.1
0.1 <u>N</u>	3.0	10.6	3.3	10.4

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