

## POTASSIUM FIXATION

# Differential Fixation of Potassium from Incorporations Of Metaphosphate and Sulfate in Two Soils

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The experimental objective was to determine the fate of the potassium of full and divided incorporations of a potassium metaphosphate fertilizer and potassium sulfate after 8 years' rainfall leaching from two fallowed soils, limstoned and dolomited. Potassium recovery from the additives was represented as the summation of outgo in rainwater leaching and gain in soil content of replaceable. The difference between added potassium and its recovery was designated as nonreplaceable or fixed. Over-all available—i.e., to leaching and to plant uptake—was expressed as the difference between the incorporated potassium and the amount that became fixed against aqueous and reagent extractions. The effects resultant from the five annual 200-pound inputs of potassium oxide as the metaphosphate fertilizer and as potassium sulfate were normal and similar in each soil. In contrast, every 1000-pound single input of potassium oxide as metaphosphate gave a high recovery and small fixation of potassium, whereas half of the corresponding inputs of the potassium of the sulfate became fixed, in nonreplaceable state in mineralized form. These relationships were not altered by incorporations of limestone or dolomite. The findings point to the economy of successive incorporation of potassium at rational rates and the wastage from single heavy-rate incorporations.

IN SIX LYSIMETER INVESTIGATIONS of the fate of potassium from incorporations of various carriers in uncropped limstoned and dolomited soils (8, 10-13, 17, 18) the potassium leachings from additive salts were determined through analyses of the periodic collections of rainwater drainage and the over-all retentions were computed, without distinction as to proportions retained in replaceable and nonreplaceable forms.

In the immediately preceding lysimeter experiment (13) the behavior of incorporations of a highly concentrated potassium metaphosphate fertilizer (25) was compared with the behavior of parallel incorporations of potassium sulfate through analyses of the 8-year rain-water leachings from the two materials in two soils, with and without limestone and dolomite. The leachings of potassium from the five annual inputs of two potassic materials were almost identical. However, there were decided disparities between those direct recoveries and the corresponding recoveries from the single 1000-pound incorporations of the two potassic materials. Retentions of additive potassium were reported then as "recoveries" which represented the differences be-

tween input and its net outgo and there was no attempt to differentiate as to the forms in which the additive potassium remained after 8 years (13).

In the studies now reported, the behavior of the potassium from the metaphosphate fertilizer, and that from the sulfate, is accounted for in Tables III and IV. The designation "Recovery" represents summation of the potassium carried by the leachings and that remaining as "Final Replaceable" in the soil. The proportions of the inputs of potassium not accounted for as recovery are the proportions that became "fixed" or "mineralized." The expression "over-all availability" connotes the percentages of the quantities of the additive potassium that did not become fixed. The equations indicate the reactions responsible for the difference between the behavior of the potassium of the metaphosphate and that of the sulfate.

### Experimental Conditions And Techniques

After the Hartsells fine sandy loam and the Fullerton silt loam of the previous lysimeter experiment (12, 13) had been exposed 8 years to the leachings from

406.5 inches of rainfall, the lysimeter-contained soils were dried and reserved for the laboratory studies reported here. Initial and final contents of exchangeable cations of the two untreated soils are recorded in Table I, and initial and final pH values for the controls and pH finals for the treated soils are given in Table II. The details of the full-depth incorporations of the metaphosphate fertilizer, potassium sulfate, limestone, and dolomite are given in groups B and C of Tables III and IV. The data for quantities incorporated, and determinations of potassium as  $K_2O$  in drainages and in soils, are in terms of pounds per 2,000,000 pounds of soil, moisture-free basis, unless excepted for expression of percentage values in Tables III to VI.

The acidic metaphosphate fertilizer was a TVA product (25). It contained 34.9% of potassium oxide and phosphorus in equivalence to a 51.6% content of phosphorus pentoxide, of which 29%, or actual of 14.96%, was as orthophosphate. The limestone comprised 98.5% calcium carbonate and the dolomite was composed of 51.5% calcium carbonate and 37% magnesium carbonate; both stones were finer than 100-mesh and virtually devoid of potassium.

**Table I. Exchangeable Cation Contents of Untreated Soils before and after Exposure to 8 Years' Rain-Water Leaching**

Determination, Meq. <sup>a</sup>	Hartsells Fine Sandy Loam		Fullerton Silt Loam	
	Initially	After 8 years	Initially	After 8 years
Calcium	1.50	0.75	2.18	1.32
Magnesium	0.22	0.14	0.32	0.22
Potassium	0.14	0.08	0.14	0.06
Hydrogen <sup>b</sup>	5.20	5.50	4.00	4.50
Exchange capacity <sup>c</sup>	7.06	6.47	6.64	6.10

<sup>a</sup> Meq. per 100 grams of dry soil.

<sup>b</sup> Difference between summation of Ca, Mg, and K and exchange capacity.

<sup>c</sup> By ammonium acetate extraction at pH 7.0.

**Table II. Final pH Values of Two Soils**

Eight years after incorporations of K metaphosphate fertilizer and K sulfate in lysimeters, with and without limestone or dolomite

Group	Incorporations		pH	
	Potassium <sup>a</sup>	Liming <sup>b</sup>	Hartsells	Fullerton
A	None	None	4.88 <sup>c</sup>	5.40 <sup>d</sup>
		Limestone	6.00	6.02
		Dolomite	6.03	6.05
B	K <sub>2</sub> SO <sub>4</sub> , 5 × 200	None	4.93	5.32
		Limestone	5.97	6.00
	K <sub>2</sub> SO <sub>4</sub> , 1 × 1000	None	4.92	5.30
		Limestone	5.97	5.95
C	KPO <sub>3</sub> , 5 × 200	None	5.05	5.42
		Limestone	6.00	6.02
		Dolomite	6.14	6.04
	KPO <sub>3</sub> , 1 × 1000	None	5.13	5.47
		Limestone	6.10	6.02
		Dolomite	6.02	6.02

<sup>a</sup> As pounds K<sub>2</sub>O per 2,000,000 pounds of soil.

<sup>b</sup> At rates of 5000 and 2775 pounds CaCO<sub>3</sub> equivalence per 2,000,000 pounds of soil for Hartsells and Fullerton soils, respectively, moisture-free basis.

<sup>c</sup> Initial pH 5.0.

<sup>d</sup> Initial pH 5.6.

Potassium contents of the eight annual rain-water drainages had been determined by means of the platinum-iodide colorimetric procedure (2, 27). The "replaceable" potassium contents shown in Tables III and VI were obtained through overnight extractions of ammonium acetate (pH 7) and subsequent leachings from 10-gram charges of 1-mm. air-dried soils. The acetate extracts were evaporated to dryness, and the resultant residues were calcined at 500° C. The calcines were dissolved in 50-ml. of 0.2N hydrochloric acid, and filtered through paper and sintered glass, according to suggestions by Fielders *et al.* (4), and the K<sub>2</sub>O values were determined in the hydrogen-oxygen flame of the Beckman DU spectrophotometer flame attachment.

### Analytical Findings

#### Induced pH Changes

The milliequivalent values given in Table I show that the untreated control soils suffered decreases in the stores of exchangeable calcium, magnesium, and potassium, with increases in exchangeable hydrogen content and attendant decreases in exchange capacity. The final pH values for the unlimed, limed, and dolomited controls of each soil and for the potassium

metaphosphate—and potassium sulfate—fortified soils, alone and with either limestone or dolomite, are recorded in Table II. The leachings of cations from the supplies native to the unlimed controls were offset by the increments from rain waters, and, therefore, the untreated control soils showed little change in pH values after 8 years' exposure.

In general, the 200-pound-per-annum inputs of K<sub>2</sub>O exerted but little effect upon the ultimate pH values in the unlimed soils. Those inputs and the single 1000-pound inputs of K<sub>2</sub>O as phosphate, and as sulfate, did not differ widely in their effects upon final pH values in the limed and dolomited soils. However, the sulfate incorporations induced pH values somewhat lower than those induced by the corresponding incorporations of the metaphosphate, although the outgo of calcium and magnesium from the phosphated soils had been found to be much greater than such outgo from the soils that contained the inputs of potassium sulfate (73).

**Potassium** The heading "recovery" in Tables III and IV connotes the summation of two directly determined values—the 8-year outgo of potassium and the content of replaceable—whereas in the report on the preceding lysimeter experiment (73), it con-

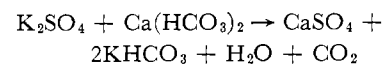
noted solely the quantities of potassium in the leachings. "Amounts fixed" defines the differences between the values for recovery and the respective combinations of replaceable of the control soils and the 1000-pound input of K<sub>2</sub>O. "Over-all available" expresses the percentage of the incorporated potassium that did not become fixed.

Because of the leachings from the native supplies of potassium, the Hartsells and Fullerton controls of groups A in Tables III and IV suffered decreases of 43 and 50% in the stores of replaceable potassium present at the beginning of the experiment. The limestone and dolomite incorporations effected appreciable decreases in the outgo of potassium from the untreated soils, in accord with other findings as to effects from incorporations of calcic, magnesian, and dolomitic materials (6, 8, 9, 14-17, 20). However, with each diminution in outgo of potassium from either a limed or a dolomited soil, there was an accumulation of replaceable potassium.

Largest recovery of potassium from the incorporated sulfate in each soil of group B, alone and with limestone, was from the five 200-pound annual inputs of K<sub>2</sub>O (Tables III and IV). However, the limestone-induced diminutions in potassium outgo were more than offset through the attendant increases in replaceable potassium in both soils; but those two phenomena did not register conclusive indications for potassium fixation.

Potassium recovery from each 1000-pound single input of K<sub>2</sub>O as sulfate in the unlimed soils was decidedly less than the recovery from the five 200-pound annual inputs. The fixations of potassium from the annual inputs in Hartsells and Fullerton soils were, respectively, only a third and a fifth as great as the fixations from the single inputs of potassium sulfate. The substantial diminutions in the recoveries of potassium from the four cases of single input of the sulfate foretold the four high fixations that occurred in the unlimed and limed soils, as graphed in Figures 1 and 2 for Hartsells and 3 and 4 for Fullerton. Here, the high fixations of potassium from the single inputs of the sulfate in the unlimed soils were as great as those in the limed soils.

Because fixations of potassium from the sulfate incorporations were more than half of the inputs, the result could not be accounted for through assumption of the direct reaction indicated by the possible equation



Such a transition of the single input of the sulfate would have resulted in a ready outgo of potassium, one similar to the high percentage outgo in the leach-

**Table III. Fate of Potassium Incorporated as Metaphosphate Fertilizer and as Sulfate**

After 8-year action of rain waters<sup>a</sup> in limestoned and dolomited Hartsells fine sandy loam

Group	Incorporations		Fate of Potassium, Pounds of K <sub>2</sub> O per 2,000,000 Pounds of Soil, from 1000-Pound Inputs				Over-all Available <sup>e</sup> , % <sup>d</sup>	
	K <sub>2</sub> O, lb.	Liming <sup>b</sup>	Outgo in drainage	Final replaceable	Recovery	Amounts Fixed		
						Lb. <sup>c</sup>	% <sup>d</sup>	
A	None	None	104	120	224	..	..	..
		Limestone	53	157	210	..	..	..
		Dolomite	44	157	201	..	..	..
B	K <sub>2</sub> SO <sub>4</sub> , 5 × 200	None	864	169	1033	191	19.1	80.9
		Limestone	712	313	1025	185	18.5	81.5
	K <sub>2</sub> SO <sub>4</sub> , 1 × 1000	None	578	133	711	513	51.3	48.7
		Limestone	416	241	657	553	55.3	44.7
C	KPO <sub>3</sub> , 5 × 200	None	877	217	1094	130	13.0	87.0
		Limestone	638	362	1000	210	21.0	79.0
		Dolomite	615	373	988	213	21.3	78.7
	KPO <sub>3</sub> , 1 × 1000	None	982	181	1163	61	6.1	93.9
		Limestone	741	301	1042	168	16.8	83.2
		Dolomite	795	337	1132	69	6.9	93.1

<sup>a</sup> Total 8-year rainfall was 406.5 inches.

<sup>b</sup> At rate of 5000 pounds CaCO<sub>2</sub> equivalence per 2,000,000 pounds of soil, moisture-free basis.

<sup>c</sup> Difference between recoveries of K<sub>2</sub>O and sum of corresponding control values and 1000-pound inputs.

<sup>d</sup> Percentage of 1000-pound input. (Respective base-pound values were 1224, 1210, and 1201 pounds of K<sub>2</sub>O for no additions, limestone, and dolomite.)

<sup>e</sup> Percentage of each 1000-pound, divided or single, input of K<sub>2</sub>O that did not become fixed.

ings from the corresponding input of the metaphosphate; but the resultant inhibited outgo of potassium from the sulfate showed that the suggested reaction did not occur. Because of the fixation of more than half of the potassium from each of the single 1000-pound inputs of K<sub>2</sub>O as sulfate—alone and with limestone—the relatively small effects that the sulfate exerted upon outgo of calcium and magnesium (73, pp. 74, 75), and only fractional leachings of the sulfate ion (73), the high concentration of the single incorporations of potassium sulfate must have engendered Ca-K-SO<sub>4</sub> complexes that caused the high fixations of potassium.

The leachings of potassium from the annual inputs of the metaphosphate fertilizer of groups C were similar to the leachings of potassium from the sulfate in the unlimed soils, but the phosphate induced somewhat larger increases in replaceable potassium and somewhat smaller fixations (Figures 1 and 3). In the limestoned and dolomited soils the annual incorporations of phosphate caused substantial decreases in the outgo of potassium, with concomitant gains in replaceable potassium and resultant increases in recovery. The two limestones also caused significant enhancements in the amounts of potassium fixed from the annual inputs of metaphosphate in both soils. However, each fixation from a phosphate annual in the Fullerton soil, was decidedly less than the corresponding fixation in the more acidic Hartsells soil (Figures 1 to 4).

Limestone caused the only significant increase in the fixation from the single 1000-pound input of the K<sub>2</sub>O of the metaphosphate in the Hartsells soil, but neither limestone nor dolomite showed significant effect upon potassium retention from the phosphate in the Fullerton soil.

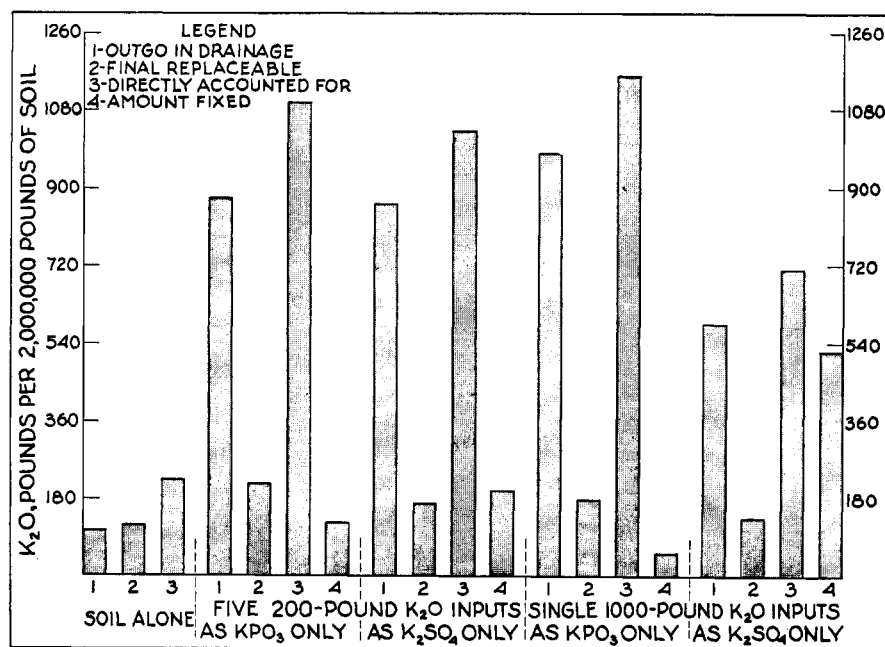
The repression that the single full in-

corporation of the phosphate had caused in the leachings of calcium from the unlimed Hartsells soil was many times the meager repression that the incorporated sulfate exerted upon calcium outgo. In the limestoned soil, however, the phosphate and sulfate induced, respectively, decreases of 636 and 120 pounds in calcium outgo as calcium carbonate equivalence (73). The phosphate and sulfate induced corresponding repressions of 333 and 32 pounds in calcium outgo (calcium carbonate equivalent) from the unlimed Fullerton soil, against the 603- and 50-pound repressions in the outgo of calcium from the limestoned Fullerton soil. Although the incorporated limestone caused a build-up of exchangeable calcium in both soils, those built-up contents did not restrain the major fixations of potassium from the sulfate incorporations, either annual or single.

The minor percentage retention of potassium from the 1000-pound input of K<sub>2</sub>O as metaphosphate cannot be accounted for as occurring in the manner attributed to the major retention from the equivalent input of sulfate. Because a fraction of the phosphorus content of the metaphosphate fertilizer was already in ortho form, and because its metaphosphate content was subject to hydrolytic transition to orthophosphate (3, 5, 7, 19, 24), the initial and engendered potassium acid phosphate of the metaphosphate reacted with the calcium compounds of the soil to form dicalcium phosphate and thereby caused substantial decreases in the leachings of calcium (73). Because of the larger

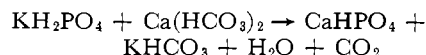
**Figure 1. Fate of potassium from 1000-pound inputs of K<sub>2</sub>O per 2,000,000 pounds of soil**

Through five 200-pound annual incorporations and single 1000-pound incorporations as K metaphosphate fertilizer and as K<sub>2</sub>SO<sub>4</sub> in Hartsells fine sandy loams after 8 years' exposure to 406.5 inches of rainfall



outgo of potassium, without concomitant outgo of orthophosphate, in the first-year leachings from the 1000-pound inputs of  $K_2O$  in the Hartsells soil, a relatively rapid conversion of meta- to orthophosphate was indicated, with less rapidity for the corresponding transition in the Fullerton soil. After 3 years, the potassium outgo from that incorporation registered a 75% transition of meta- to orthophosphate in the Hartsells soil.

The reactions responsible for the precipitations of the engendered orthophosphate can be expressed through the following equations:



The engendered dicalcium phosphate would conserve orthophosphate and diminish outgo of calcium and magnesium, while liberating leachable potassium bicarbonate. This phenomenon is indicated by the 88 and 84% net leachings of potassium from single inputs of the metaphosphate in the unlimed Hartsells and Fullerton soils, respectively, and also by the corresponding leachings of 69 and 84% from the two limed soils (Tables III and IV).

The foregoing explanation is supported by the findings (Table V) for phosphorus pentoxide outgo and residues from the twelve metaphosphate incorporations in the two soils. The largest net outgo of phosphorus pentoxide from the 1478-pound input constant was 1.99 pounds for Hartsells and 3.63 pounds for Fullerton. Hence, the mean of the six reten-

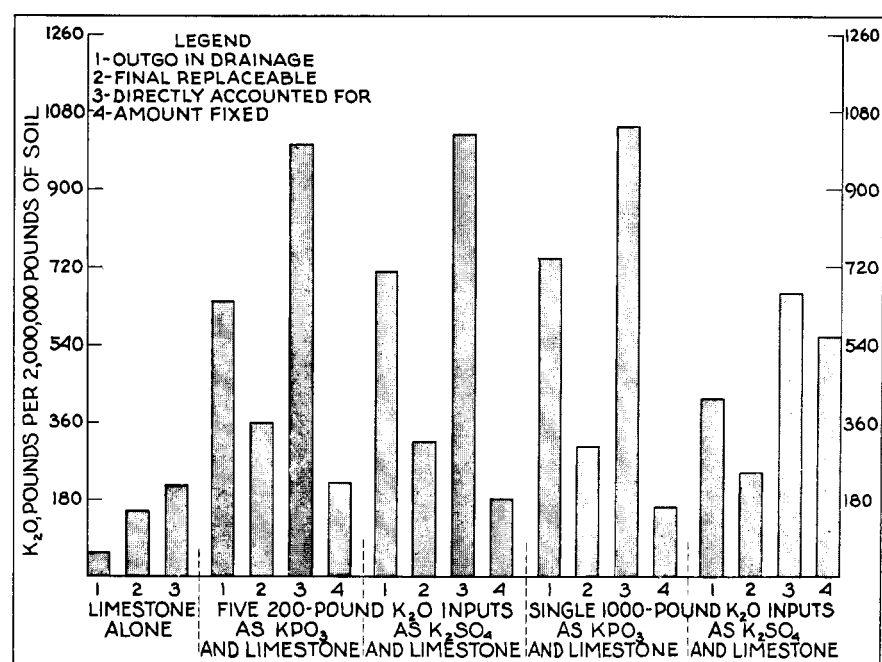


Figure 2. Fate of potassium from 1000-pound inputs of  $K_2O$  per 2,000,000 pounds of soil

Through five 200-pound annual incorporations and single 1000-pound incorporations as K metaphosphate fertilizer and as  $K_2SO_4$  in limed Hartsells fine sandy loam, after 8 years' exposure to 406.5 inches of rainfall

tions of phosphorus pentoxide by the Hartsells soil and the six by the Fullerton soil were 1476 pounds and 1474 pounds, respectively, or 99.8 and 99.75% of the 1478-pound phosphorus pentoxide input that was constant to the soils in the twelve lysimeters.

With one exception, the two liming materials caused increases in the outgo of

phosphate from the metaphosphate in both soils, but the potassium sulfate appeared to cause decreases in the leachings of phosphate.

As additional evidence of the meager migration of either meta- or orthophosphate, in contrast to the high percentage outgo of the associated potassium, phosphate residues in the 26 soil systems were determined directly and are reported in Table V. A 10-gram charge of each final soil of the lysimeter experiment was digested in aqua regia overnight, the resultant solution-suspension was filtered, the filtrate was evaporated to free it of silica, and its phosphorus pentoxide content was determined volumetrically. The differences between the phosphorus pentoxide dissolved from the no-metaphosphate controls of the two soils (means of 0.042 and 0.067%) and the corresponding extractions of the phosphated soils (means of 0.113 and 0.132%) register retentions of 1420 and 1300 pounds of phosphorus pentoxide, or 96.7 and 88% from the 1478-pound common input, in the Hartsells and Fullerton soils.

The foregoing values for phosphate outgo in the drainage waters are virtually absolute and register recoveries that were mere fractions of 1% of the phosphate input. The small, yet larger, indications from the acid extractions of the phosphate residues may be due to the errors of the small samplings and to incomplete extractions. However, the two direct analytical procedures establish the near-complete retentions of the additive

Table IV. Fate of Potassium Incorporated as Metaphosphate Fertilizer and as Sulfate

After 8-year action of rain waters<sup>a</sup> in limed and dolomited Fullerton silt loam

Group	$K_2O$ , lb.	Liming <sup>b</sup>	Fate of Potassium, Pounds of $K_2O$ per 2,000,000 Pounds of Soil, from 1000-Pound Inputs				Over-all Available <sup>e</sup> , % <sup>d</sup>	
			Outgo in drainage	Final replaceable	Recovery	Amounts Fixed Lb. <sup>c</sup> % <sup>d</sup>	Available <sup>e</sup> , % <sup>d</sup>	
A	None	None	184	108	288	..	..	..
		Limestone	151	120	273	..	..	..
		Dolomite	152	157	309	..	..	..
B	$K_2SO_4$ , 5 × 200	None	1004	181	1185	103	10.3	89.7
		Limestone	944	241	1185	88	8.8	91.2
	$K_2SO_4$ , 1 × 1000	None	589	145	734	554	55.4	44.6
		Limestone	589	169	758	515	51.5	48.5
C	$KPO_3$ , 5 × 200	None	1011	241	1252	36	3.6	96.4
		Limestone	875	289	1164	109	10.9	89.1
		Dolomite	969	253	1222	87	8.7	91.3
	$KPO_3$ , 1 × 1000	None	1021	193	1214	74	7.4	92.6
		Limestone	988	217	1205	68	6.8	93.2
		Dolomite	994	229	1223	86	8.6	91.4

<sup>a</sup> Total 8-year rainfall was 406.5 inches.

<sup>b</sup> At rate of 2775 pounds  $CaCO_3$  equivalence per 2,000,000 pounds of soil, moisture-free basis.

<sup>c</sup> Differences between recoveries and sum of corresponding control values and 1000-pound inputs.

<sup>d</sup> Percentage of 1000-pound input. (Respective base-pound values are 1288, 1373, and 1309 pounds of  $K_2O$  for no additions, limestone, and dolomite.)

<sup>e</sup> Percentage of each 1000-pound, divided or single, input of  $K_2O$  that did not become fixed.

phosphate in the twelve phosphated soil systems and point to the development of recalcitrant "mineralized" forms in the 8 years of exposure and aging.

**Potassium Metaphosphate vs. Potassium Sulfate**

In the comparisons between the reactivities of the phosphate and the sulfate in the unlimed soils of groups B and C of Tables III and IV, maximal recoveries of potassium were from the metaphosphate. The cumulations of replaceable potassium from the annual inputs of the phosphate in the unlimed soils exceeded the cumulations from the corresponding inputs of the sulfate; and the corollary fixations of potassium from the metaphosphate annuals in the unlimed soils were substantially less than the "amounts fixed" from the sulfate annuals. Moreover, the fixations of potassium from the 1000-pound single inputs of  $K_2O$  as the sulfate in the unlimed Hartsells and Fullerton soils were 8.4 and 7.5 times the fixations of potassium from the corresponding incorporations of the metaphosphate.

The substantial fixations of potassium from the annual inputs of the sulfate were not increased by accompanying incorporations of limestone in the two soils, and this holds also for the major fixations of potassium from the 1000-pound inputs of  $K_2O$  as sulfate in the two soils, as in groups B of Tables III and IV.

The fixations of potassium from all inputs of the metaphosphate and the sulfate in both soils are summarized in Table VI.

When the high percentage of potassium recoveries from the metaphosphate

are related to the earlier findings that the metaphosphate caused attendant decreases in the leachings of calcium and magnesium, and then contrasted to the smaller recoveries of potassium from the single 1000-pound incorporations of  $K_2O$  as the sulfate, and with little effect upon calcium and magnesium outgo, and contrasted also to the ready leaching of potassium sulfate from the limed and dolomited soils of two 10-year lysimeter experiments (10, 11), it seems certain that development of mineralized combinations of calcium, potassium, and sulfate are responsible for the high joint retentions of potassium and sulfate from the 1000-pound inputs of  $K_2O$  in the present experiment.

**Limestone vs. Dolomite Effects On Potassium of Metaphosphate Fertilizer**

Because of the similarity in the repressions that limestone and dolomite exerted upon potassium outgo from its sulfate in earlier experiments (10, 18), the limestone and dolomite are compared only as to their effects upon the potassium of the potassium metaphosphate fertilizer. The two types of limestone induced similar effects upon the five 200-pound annual inputs of  $K_2O$  in the Hartsells soil. Dolomite proved less repressive than limestone upon outgo of potassium from the 1000-pound single inputs of group C, developed more replaceable potassium, and caused virtually no increase in potassium fixation. Limestone proved more repressive upon outgo of potassium, induced less cumulation of replaceable potassium, and caused a 10% enhancement over the potassium

fixation that occurred in the unlimed soil.

Dolomite was less repressive than limestone upon outgo of potassium from the annual inputs of the metaphosphate in the Fullerton soil; it induced less cumulation of replaceable potassium and caused slightly less fixation. However, dolomite and limestone exerted similar effects upon the behavior of the potassium of the 1000-pound inputs of  $K_2O$  as metaphosphate in group C of Table IV.

**Discussion**

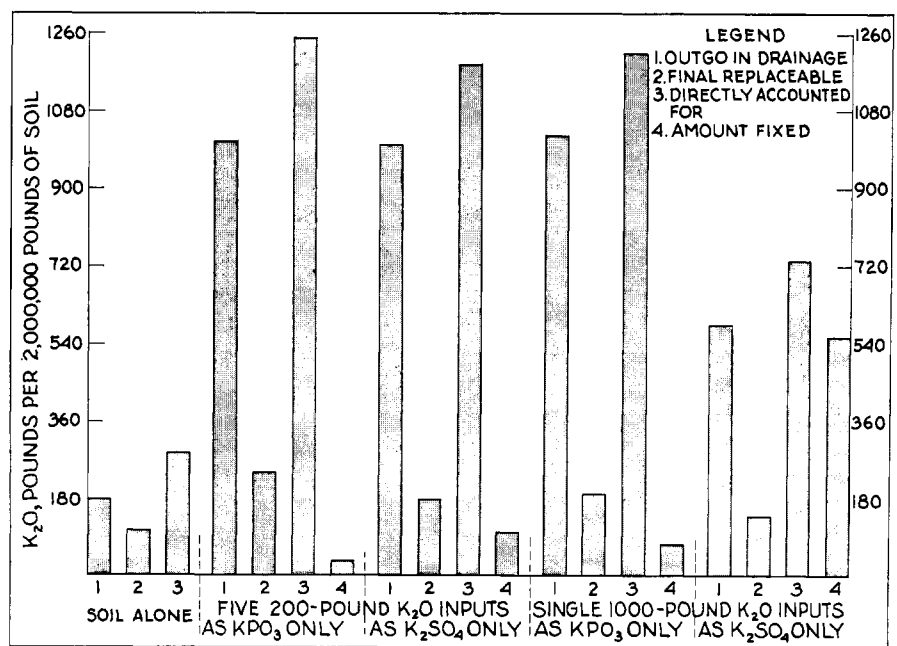
Obviously, different phenomena are responsible for the disparity in the large fixations of potassium from the 1000-pound single inputs of  $K_2O$  as metaphosphate and as sulfate in the two soils, in contrast to the smaller fixations from the five 200-pound annual incorporations of the two potassic materials, especially in the Fullerton silt loam. The effect of the mass of the highly soluble sulfate is reflected by the mean of 53.4% for the four determinations of the fixations of potassium from the 1000-pound inputs of  $K_2O$  as sulfate in the two soils, and by the mean of only 8.75% for the six cases of fixation from the corresponding inputs as the phosphate. The mean values for all fixations of potassium from all of the incorporations into the Hartsells fine sandy loam and Fullerton silt loam were 22.9 and 16.5%, respectively.

The fixations of potassium from the 1000-pound single inputs of  $K_2O$  as the sulfate in the two soils, unlimed and limed, were 53.35 and 53.40%, respectively. Those fixations of potassium were accompanied by abnormal retentions of sulfate, which did not ensue from the 200-pound annual inputs of  $K_2O$ . The outgo of potassium from the five annual inputs of the metaphosphate and sulfate in the two soils were close to 80% of the input. In contrast, only 44% of the potassium of the single input of the sulfate was leached from the two unlimed soils, whereas 86% of the potassium of the single incorporations of metaphosphate was leached, three fourths of the outgo having occurred in the initial 3 years.

Separate comparisons show percentages of 81.2 and 81.6 for over-all available, or percentages of the additive potassium that were not fixed, from the  $5 \times 200$ -pound incorporations as sulfate and metaphosphate in the unlimed and limed Hartsells soil. In contrast were the respective values of 46.7 and 90.1% for over-all available from the single 1000-pound input of  $K_2O$  as sulfate and phosphate in the Hartsells soil—unlimed, limed, and dolomited. Similar comparisons show values of 90.5 and 92.3% for over-all available from the  $5 \times 200$ -pound inputs of  $K_2O$  as potassium sulfate and metaphosphate in the Fullerton soil, against

**Figure 3. Fate of potassium from 1000-pound inputs of  $K_2O$  per 2,000,000 pounds of soil**

Through five 200-pound annual incorporations and single 1000-pound incorporations as K metaphosphate fertilizer and as  $K_2SO_4$  in Fullerton silt loam, after 8 years' exposure to 406.5 inches of rainfall



which were percentages of 44.6 and 92.6 for the quantities of potassium that were not fixed from the single inputs of sulfate and metaphosphate, respectively, in that soil, unlimed. The highest quantity for over-all available potassium from the several incorporations of the metaphosphate fertilizer was 92.9% in the Hartsells soil and 93.2 in the Fullerton soil.

Obviously, the fate of the potassium incorporated as metaphosphate and as sulfate will be governed by the dissolubility and precipitative properties of the carriers, by rate and mode of input, by duration after incorporation, by quantity and nature of the alkali-earth bases of the receiving soil, and by the effects of supplements of limestone and dolomite.

A laboratory study of the transitions of the potassium of additive sulfate into replaceable and nonextractable combinations was reported by Shaw and MacIntire (22). Through successive aqueous and ammonium acetate extractions, they obtained complete recoveries of additive potassium from 10-gram charges of a red clay subsoil that contained 100- and 500-mg. inputs of  $K_2O$  as potassium sulfate. But the same analytical technique registered only

fractional recoveries of the potassium in the leaching and extraction of like additions in a calcareous soil. Recently, Ayres and Hagihara reported upon "the ability of the soils of the water regions to retain applied potassium against the leaching action of water" (7), and concluded that no fixation of potassium resulted from surface applications of the sulfate and a metaphosphate fertilizer (7, p. 3, 25) at the rate of 1250 pounds of  $K_2O$  per acre surface. Volk (23) and Shaw and MacIntire (22) also reported that potassium fixation did not occur in soils that were kept moist.

In contrast to the findings of Ayres and Hagihara are the high fixations of potassium reported by Volk (23) and the 50 to 79% fixations that Shaw and MacIntire (22) encountered in a calcareous soil that had been fortified through incorporations of potassium sulfate. In contrast, also, are the fixations of 51 and 55% of the potassium from the 1000-pound inputs of  $K_2O$  as sulfate in the unlimed Hartsells and Fullerton soils, and corresponding fixations of 55.3 and 51.5% from the sulfate inputs in those two soils, limed (Tables III and IV).

In finding that "leaching removed all of the 1250-pound ( $K_2O$ ) applications of potassium per acre from the surface foot of the  $KCl$ - and  $K_2SO_4$ -treated soils" Ayres and Hagihara (7) analyzed leachates from successive increments of 2.5 inches of water to totals of 90 to 100 inches. Apparently, they did not allow the soil columns to become dry between percolations, a condition the present authors have found conducive to retention and fixation of potassium from additions in solution. Moreover, Volk (23) reported that "alternate wetting and drying of soils treated with soluble potassium salts caused rapid fixation of the potassium in a nonreplaceable form." Such a succession of moist and dry conditions was natural to the Tennessee soils of the 8-year lysimeter experiment. Volk observed also that "when these soils were kept continuously moist, very little fixation of this kind took place."

Because of the brevity of the laboratory leaching experiment reported by Ayres and Hagihara (7), in contrast to the duration of the 8-year lysimeter study, the findings from the two experiments would not be expected to coincide.

All incorporations of potassium metaphosphate, the 1000-pound additions of  $K_2O$  in particular, caused substantial diminutions in outgo of calcium and magnesium from the two soils—unlimed, limed, dolomited (13)—in contrast to little, if any, exchange between the potassium of the additive sulfate and soil content of calcium and magnesium.

Two distinctive facts stand out from comparison between earlier data for outgo of potassium (13) and the findings reported here as to the transitions of water-soluble potassium into replaceable and fixed forms. Both carriers yielded high "recovery" of potassium and relatively small fixations from the five annual incorporations. The quantities of potassium not fixed, or over-all available, from those incorporations did not differ widely for potassium metaphosphate and potassium sulfate in each soil, the larger percentages of the unfixed potassium being those from the Fullerton silt loam.

In contradistinction, decidedly different results obtained when the two potassic materials were incorporated in parallel through single inputs at the rate of 1000 pounds of  $K_2O$  per 2,000,000 pounds of soil. The high percentage recoveries of potassium and the small fixations that attended such incorporations of the metaphosphate fertilizer were opposite to the substantial fixations of both potassium and sulfate from the parallel inputs of potassium sulfate.

A practical application of the findings is that repetitive rational-rate incorporations of the two carriers of potassium would be preferable to heavy-rate incorporations at extended intervals. Incorporations of the two potassium materials at the rate of 1000 pounds of  $K_2O$

**Table V. Eight-Year Outgo and Residues of  $P_2O_5$  from Incorporations of Potassium Metaphosphate Fertilizer and Potassium Sulfate**

After 8 years' exposure to action of rain waters<sup>a</sup> in two soils

Group	Incorporations		Hartsells Fine Sandy Loam		Fullerton Silt Loam		
	Potassium <sup>b</sup>	Liming <sup>c</sup>	$P_2O_5$ outgo, lb.	$P_2O_5$ residue <sup>d</sup> , %	$P_2O_5$ outgo, lb.	$P_2O_5$ residue <sup>d</sup> , %	
	A	None	None Limestone Dolomite	0.538 0.545 0.396	0.041 0.040 0.045	0.314 0.598 0.414	0.062 0.071 0.068
B	$K_2SO_4$ , 5 × 200	None Limestone	0.252 0.389	0.043 0.043	0.140 0.559	0.068 0.081	
		$K_2SO_4$ , 1 × 1000	None Limestone	0.236 0.398	0.044 0.040	0.398 1.459	0.067 0.067
			Av.	0.042		0.067	
	C	$KPO_3$ , 5 × 200	None Limestone Dolomite	0.614 2.487 2.411	0.113 0.115 0.116	2.121 2.581 1.642	0.138 0.138 0.118
$KPO_3$ , 1 × 1000			None Limestone Dolomite	1.159 1.456 1.557	0.113 0.108 0.114	2.851 3.593 4.085	0.133 0.129 0.135
					Av.	0.113	

<sup>a</sup> Total rainfall was 406.5 inches.

<sup>b</sup> As 5 × 200 and 1000 pounds of  $K_2O$  per acre, full depth; soils from all lysimeters were removed and mixed when each 200-pound annual addition was incorporated.

<sup>c</sup> At rates of 5000 pounds  $CaCO_3$  equivalence for Hartsells and 2775 pounds for Fullerton

<sup>d</sup> By direct analyses of soil at termination of experiment.

**Table VI. Comparative Fixations of Potassium, as Means for the Experimental Potassium-Fortified Systems**

Incorporations	Fixations as $K_2O$ per 2,000,000 Pounds of Soil <sup>a</sup>			
	In Hartsells Soil		In Fullerton Soil	
	Lb.	% <sup>b</sup>	Lb.	% <sup>b</sup>
$K_2SO_4$ , two 5 × 200 units <sup>c</sup>	188	18.8	96	9.6
$K_2SO_4$ , two 1 × 1000 units <sup>c</sup>	533	53.3	535	53.5
$KPO_3$ , three 5 × 200 units <sup>d</sup>	184	18.4	77	7.7
$KPO_3$ , three 1 × 1000 units <sup>d</sup>	99	9.9	76	7.6

<sup>a</sup> Moisture-free basis.

<sup>c</sup> Alone and with limestone.

<sup>b</sup> Of 1000-pound input.

<sup>d</sup> Alone, with limestone and with dolomite.

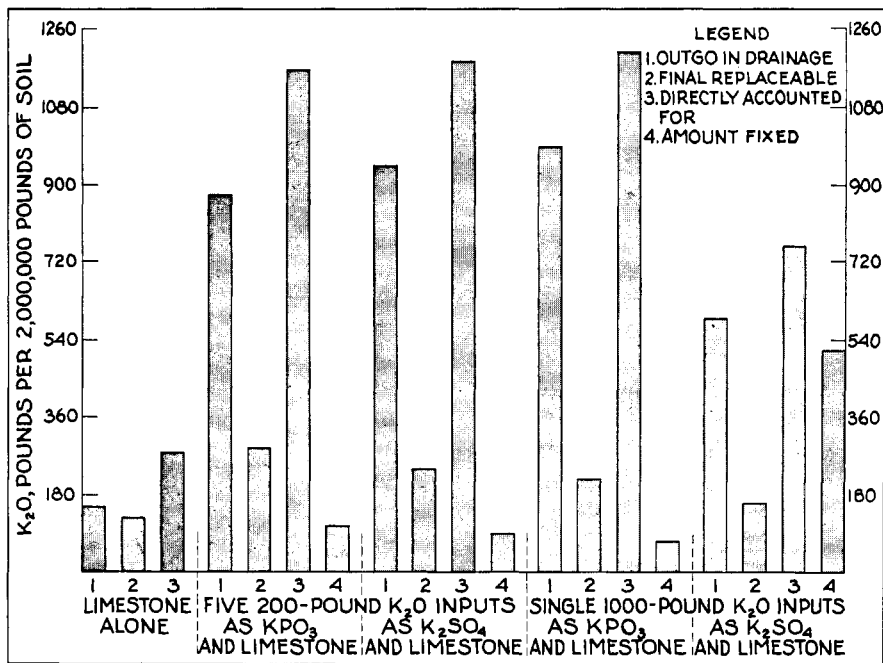


Figure 4. Fate of potassium from 1000-pound inputs of  $K_2O$  per 2,000,000 pounds of soil

Through five 200-pound annual incorporations and single 1000-pound incorporations as K metaphosphate fertilizer and as  $K_2SO_4$  in limestoned Fullerton silt loam, after 8 years' exposure to 406.5 inches of rainfall

per acre would not be advisable. The metaphosphate would induce quick diminution of the soil supplies of calcium in exchangeable forms other than phosphate and its potassium content would be wasted into the drainage waters from fallow soils in humid regions and through luxury consumption by crops, whereas corresponding incorporations of potassium sulfate would result in a molecular fixation of potassium and sulfate that would prevent their becoming readily available as nutrients to plants.

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#### Summary

Comparable recoveries of the potassium from five 200-pound annual incorporations of  $K_2O$  as a metaphosphate fertilizer and as sulfate were determined through combinations of 8-year rain-water leachings and amounts conserved as replaceable in two soils, unlimed and limestoned; and amounts of corollary fixations were established.

In contrast, the potassium leachings and gains in replaceable from single 1000-pound inputs of  $K_2O$  as metaphosphate fertilizer exceeded greatly such leachings and gains from parallel inputs of potassium sulfate in the two soils, unlimed and limestoned. The mean of the fixations of potassium from the four cases of 1000-pound inputs of

$K_2O$  as the sulfate was 53.4% in contrast to the 8.7% mean for the six cases of phosphate inputs.

Although limestone and dolomite caused decreases in the leachings of potassium, with and without incorporations of potassium, they also caused cumulations of replaceable potassium in the soils. The two types of limestone induced comparable effects upon the single inputs of potassium metaphosphate in both soils, although limestone induced somewhat greater fixation of potassium in the Hartsells soil.

Transitions of the single incorporations of potassium metaphosphate into potassium acid phosphate and potassium carbonate outgo are postulated to account for high percentage recoveries of potassium and minimal fixations of it, with substantial concomitant decreases in outgo of calcium and magnesium.

Because of the fixations of potassium and retention of sulfate from the incorporated sulfate, without evidence of substantial exchange between additive potassium and soil calcium, it seems evident the over-all retention of the incorporated potassium sulfate was due to development of Ca-K-SO<sub>4</sub> complexes.

Comparable recoveries of potassium can be expected from 200-pound-per-acre parallel incorporations of  $K_2O$  as potassium metaphosphate and potassium sulfate in fallow soils of like characteristics and with like rainfalls. But, substantial losses of potassium from heavy-rate incorporations of potassium metaphosphate would occur in fallow soils and through luxury consumption by

vegetation, whereas half or more of the potassium of the parallel input of the sulfate would be lost because of its becoming fixed, or mineralized.

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