## THESIS

on

THE RELATION OF CALCIUM ION REQUIREMENT OF ALFALFA TO

THE CALCIUM CONTENT OF THE SOIL

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Many of the soils of the humid regions are becoming gradually depleted of essential nutrients due to leaching, crop removal and exhaustive methods of soil management. Calcium, according to Higby (14) is the plant nutrient that is lost by leaching in greatest quantities. Calcium is required by many plants in large amounts (16). It is conceivable that this loss of calcium in a soil may result in development of soil acidity which will in turn affect the vegetation by not being present in large enough amounts to supply the crop needs. The virgin soils are recognized to generally contain larger amounts of calcium than soils that have been cropped for several decades. Through leaching with acids such as carbonic and sulfuric and cropping, much calcium is removed, allowing hydrogen ions to replace the calcium absorbed in exchangeable form on the ultra-clay complex, thus causing the formation of a soil unsaturated with bases (10). The soils of Kentucky blue grass district occupy a position in which limestone was once prevalent. The soil present there now is of residual formation from the impurities of the limestone. The lime has been leached out until the soil in certain places is acid in reaction and crops growing there respond to treatment with limestone (30).

Legume plants are heavy users of calcium compared with non-legumes, as is shown by the chemical analysis of the plants (16) and the nutritional studies that have been carried on. Some legumes which thrive in soils whose reaction is definitely on the acid side, such as soybeans, Dalea and vetch (15) required a relatively large amount of calcium to make their best growth. Alfalfa and sweet clover are less

tolerant to the hydrogen ion and require a soil which contains a relatively large amount of readily available calcium.

Very little work has been done in the past for the purpose of determining a suitable concentration of calcium ion for plant nutrition. Some studies have been carried on in the past at the Oregon station, the results of which indicate that alfalfa requires a higher concentration of calcium than of any other essential ion in order to live or make satisfactory growth.

The object of the present investigation is to show the effect of maintaining different calcium ion concentrations upon the growth of alfalfa and the seasonal variation in water soluble calcium in field soils and in treated soils in jars. The change in replaceable calcium and in reaction of soils due to treatment is also reported.

The application of limestone to soils for the purpose of increasing crop growth has been practiced for centuries. Pliny, the Roman general, upon his return from his English campaign told how marl was being used on the soils of England (40). de Saussure in 1804 showed the absolute necessity of calcium salts in plants (32). Boussingault (2) conducted rotation experiments and analyzed carefully the plants grown and the amount of plant food removed from the soil in crops; he accounted for the amount of different nutrients applied as fertilizer and thereby drew conclusions as to gains and losses of various nutrients including calcium used by the plant. Knop (17) studied the functions of ash constituents of plants and metabolic process. He found that the plant took up a larger amount of calcium than it did of magnesium. Loew (20) found that calcium is necessary if the plant is to continue to grow after the supply in the seed has been used up. True (38) found that calcium was necessary for the formation of each new cell within the plant.

The most essential components of plants are perhaps carbon dioxide, water and certain salts containing nitrogen, sulfur, potassium, calcium, magnesium and iron (19). Some of these elements are necessary throughout the growth period such as calcium and nitrogen. Powers (28) found that sulfur is most needed by the plant during the early part of the growth period. McCall and Richards (24) found that the wheat plant required magnesium most from the time the plant was 60 days old until maturity. The calcium, phosphorus, nitrogen and sulfur requirement remained the same throughout the growth period. A trace

of boron and other "non-essential" elements in water cultures has been found of benefit (28).

Calcium is abundant in many of the rocks which are the parent material of many of our soils. Some of the minerals which contain calcium are calcite, dolomite, hornblende, augite, gypsum, apatite, plagioclase, epidote, titanite, garnet and sosite (34). The rocks containing these minerals are acted upon by acids such as carbonic, sulphuric and nitric and by agents of weathering and disintegration (28).

Hartman (13) while studying the economic use of the different nutrients for the growth of alfalfa, found that 32 parts per million of calcium were required to make satisfactory growth. The growth was benefitted some when 64 parts per million were used. Where large amounts of magnesium were present in proportion to the amount of calcium present, magnesium injury occurred. Where less than 6 parts per million of calcium were present, the plants died. He found that alfalfa required a larger concentration of calcium than it did of any other ion.

Lomanitz (21) used a solution having an ion concentration in the proportion of 2 parts of calcium nitrate, 4 parts of magnesium sulphate and two parts of mono-potassium phosphate. He believed that there was a direct correlation between the yield of crop grown and the calcium concentration of the solution.

The concentration of calcium with respect to that of magnesium can vary widely as shown by the results of Hartman (13).

However, Loew (20) obtained the best results when the calcium - magnesium ratio was 5:4. Gericke (11) pointed out two factors which were operating in magnesium injury, namely the relationship of the

calcium concentration to the magnesium concentration and the addition of salts of phosphorus containing some calcium. Reed (29) working with wheat seedlings found that toxic solutions of sodium chloride could be antidoted by 30 parts per million of calcium oxide. However, it was found that calcium rendered the sodium harmless after entrance into the plant when the concentration of calcium was two parts per million and the sodium concentration was 98 parts per million.

Where the concentration of calcium was increased, Lipman and Blair (18) found that the nitrogen content of the stalk of soybeans was increased from .615% to .791%. It is quite possible in this case that calcium conditioned the membrane for nitrogen absorption. Ginsburg and Shive (12) found a definite correlation existing between the calcium concentration of the solution and the calcium content of the plant.

Dickson (8) working with the cat plant, found that the period of development could be shortened by the further addition of calcium.

The application of different amounts of limestone to the soil did not change the reaction of the plant sap to any appreciable degree in some experiments carried on by Dustman (9).

The concentration of calcium within the soil varies with the season and the crop used. Burd (4) after a series of experiments concluded that plants had the power to reduce the calcium concentration in fertile and poor soils alike to a certain minimum and that subsequent withdrawal would be dependent upon the capacity of the soil to elaborate additional solutes. He also found that when the plant is making its greatest growth, the concentration of calcium is liable to be lowest.

Stephenson (35) studied the amount of exchange calcium on Willamette loam and on Dayton silty clay loam. These soils contained the following amounts of calcium as Ca++:

Soil	Surface	Subsurface	Subsoil	Substrata
Willamette loam	.3317%	.3714%	.3464%	.4046%
Dayton silty clay	.1134	.1306	.3654	.2394

There was a rather rapid increase in water soluble calcium in Elmira silty clay loam due to the application of varying amounts of limestone and after varying intervals of time (35). The reaction of this soil was not materially changed during the short period covered by this investigation.

The effect of nitrogen treatment on the amount of calcium in the soil water was studied by Morse (25). The average of calcium leached over a period of 5 years was as follows for each treatment:

## Treatment

P.P.M. Calcium present	NaN03 24.8	No Nitrogen 36.5	(NH4)2SO4 54.2
The reason for more than	two times as	much calcium bei	ng brought into
solution by ammonium sulp	hate as by so	dium nitrate was	perhaps due to
the hydrolysis of ammoniu	m sulphate to	sulfuric acid a	and ammonium
hydroxide.			

Calcium seems to perform various functions within the plant, such as seed production as shown by experiments with oats by Dickson (8). Breazeale (3) found that calcium had an accelerating effect on the root growth. Parker and Truog (27) supposed that one of the functions of calcium was to neutralize the organic acids within the

plant. They seemed to find that oxalic acid united with calcium carbonate according to the equation:

 $\mathrm{H_{2}C_{4}O_{2}}$  plus  $\mathrm{CaCO_{3}}$  equals  $\mathrm{H_{2}CO_{3}}$  plus  $\mathrm{CaC_{4}O_{2}}$   $\mathrm{H_{2}CO_{3}}$  equals  $\mathrm{H_{2}O}$  plus  $\mathrm{CO_{2}}$ 

Dustman (9) disagreed with Parker and Truog. He studied the effect of calcium on the reaction of the sap of tomato plants, and found that increased increments of calcium had very little effect, if any, on the reaction of the juice. Calcium aids the plant in absorbing nutrients from the solution (39). Powers (28) found that alfalfa made the best use of limited amounts of sulfate when calcium sulfate was used. Each cell within the plant is surrounded by a layer of calcium pectate which gives it rigidity (38).

The application of limestone to soils causes various chemical phenomena to take place. McIntire et al (23) found that the application of calcium to the soil conserved the soluble potash additions in a form which was probably available to the plants, yet resistant to excessive loss from leaching. By increasing the calcium concentration of the soil solution, McIntire et al (22) found that sulfur was brought into solution much more readily. Calcium is a good flocculating agent. This property is believed to be due to (10) its high atomic weight and perhaps because it is bivalent.

The concentration of the calcium ion in the soil solution may be the leading factor in maintaining a reaction suitable for plant growth. Some plants, however, can grow best in a soil or culture solution whose reaction is decidedly acid (31). Theron (37) studied the influence of reaction of the culture solution on the growth of barley, peas, cucumbers, corn and alfalfa. He found that the best growth took place at pH 4.8 to 6. Calcium comes into solution as acidity begins to develop to protect the plant.

## PLAN OF INVESTIGATION

The subject under investigation has been studied from the three points of attack as follows:

- 1. To grow Grimm alfalfa in nutrient solutions lacking calcium and study the effect of successive increments of calcium upon the growth of alfalfa.
- 2. To study the effect of season and treatment on the water soluble calcium content in soils in the field and in pots over a period of twenty-four weeks.
- 3. To determine the amount of replaceable calcium present in the soils used in part 2.

Grimm alfalfa was chosen as the plant to be used in this investigation. Four times as many seeds as were necessary were first shaken in a solution consisting of 1000 cc of distilled water, 2 grams of mercurous chloride and 5 cc of concentrated hydrochloric acid for ten minutes (6). They were then rinsed three times in distilled water. The seeds were germinated in sterilized quartz sand and were inoculated with alfalfa strain of Rhizobium leguminosarum. They were not transplanted until the 4th leaf had appeared. Only plants free from injury and uniform in size were transplanted. Four plants washed free of sand and foreign matter with distilled water were transplanted to each jar. The jars were two quart mason fruit jars covered with 3 layers of heavy brown paper and equipped with composition corks. These were autoclaved before culture solution was added. The corks had four holes and were coated with paraffin in the winter trial but the paraffin was omitted during the summer trial. Absorbent cotton was packed around each plant to hold it in position. The number of plants per jar was

reduced to three after three or four days had elapsed since transplanting. Where less than three plants were alive three or four days after transplanting, replacement was made with plants growing in the quartz sand and which were the same age and size.

The plants were grown in the college greenhouse during the winter trial so as to duplicate as nearly as possible the climatic conditions that exist out of doors during the summer season. Average day length was produced by electric light using a 1000 candle power nitrogen bulb. The different sets of cultures were moved twice a week so that all plants would receive about the same amount of light during the growth period.

The plants were grown out of doors during the summer season on a balcony where they were protected from direct sunlight during the hot part of the day. The advantage of this out door propagation was to keep away from greenhouse pests and disease and imitate natural conditions.

The hydrogen ion conventration of the culture solution was adjusted to pH 5.6 - 5.8. The solutions were renewed each week in order to maintain the concentration of calcium ion. During the week, only slight changes toward neutrality were observed in the culture solution which were adjusted by the use of .1 normal sulfuric acid. Dipotassium phosphate, mono-potassium phosphate and the addition of .1 grams per liter of potassium-acid-phthalate were used to buffer the solution.

The trial which was carried on during the winter lasted six weeks. Bacterial and fungus diseases were a menace to the experiment.

The trial which was carried on during the summer was a

duplicate of the winter trial with the exception that series No. 3 was omitted on account of the similarity of results to those in series No. 2 of the winter trial. At the end of the six weeks' growth period, photographs and data were taken which are shown in figure 1 and tables 1 and 2. In harvesting the plants, the roots were washed and rewashed in distilled water and then dried in an oven at 100 degrees Centigrade for ten hours. The dry weights of the tops and roots were determined.

The plants were grown in solutions containing varying parts per million of calcium, each series consisted of 6 jars, each holding three plants.

There were ten series of nutrient solutions which contained 240, 0, 2, 4, 6, 8, 16, 32, 64, 128, and 320 parts per million of calcium respectively. The nutrient solution to which different concentrations of calcium were added was a modification of a solution used by Powers (28). The modification consisted of reducing the concentration of the various ions and particularly of the magnesium ion, since small concentrations of calcium ion were employed in some of the series. Since

the culture solution was renewed each week, no marked change in concentration was permitted to take place. The nutrient solution consisted for the following salts which were made up in stock solutions of molar strength:

or morar screngon:	No. c	c of Molar			Parts per
		ion per		Ion Present	Million
Salt	Liter	of Soluti	ion		
KH2P04		3.33		K	130
2-4		3.33		P	103
K <sub>2</sub> HPO <sub>4</sub>		1		K	76
2 =		1		P	31
MgSO <sub>4</sub>		1		Mg	24
		1		·S	32
KNO3		4		K	156
		4		N	56
Potassium Acid Phthalat	е				100
Total concentration					710

One cc of 1% ferric tartrate per liter was used as a source of iron, because it remains in solution.

The seasonal variation of water soluble calcium in soils was studied under controlled conditions in earthenware jars and also under field conditions. The soils used for studies in jars were fallow Melbourne Silty Clay loam and fallow Willamette Silty Clay loam. Twenty pound lots of air dry soil was used in four gallon jars. The different treatments were mixed with the soil on an oilcloth sheet before being placed in jars. The different treatments consisted of:

				Treatment	Ser	ies
	Soil			Per Acre	Fallow	Cropped
Melbourne	Silty	Clay	Loam	Check 10 T. Manure	Fallow	Alfalfa
11	11	11	. 11	250# Sulfur	11	11
- 11	tt	11	11	450# Super Phosphat	e #	11
11	11	11	11	4 T. Gr. Limestone	11	11

The water soluble calcium was studied quantitatively in fallow and cropped field soils of Dayton Silty Clay Loam on the station farm,

and on fallow and cropped Chehalis Fine Sandy Loam on the east college farm. Barley and berries were the growing crops on the Dayton Silty Clay Loam and on the Chehalis Fine Sandy Loam respectively. These quantitative chemical determinations were made in duplicate according to the potassium permanganate method as outlined by Scott (33).

The study of the amount of replaceable calcium was conducted on the fallow Melbourne Silty Clay Loam and Willamette Silty Clay Loam and cropped and fallow Chehalis Fine Sandy Loam in the field under the same conditions as for water soluble calcium. The amount of calcium present in replaceable form in the check, manure, sulfur and super phosphate treated soils in jars and the soils in the field was determined by leaching with .05 normal hydrochloric acid. The amount of calcium present in the extracted solution was determined by the same method as the water soluble calcium. The amount of replaceable calcium present in the ground limestone treated soils at the close of the experimental period was determined by leaching with 10% BaCl<sub>2</sub>. The amount of calcium present in the leachings was determined by the soap titration method (7) which is more suitable for use with soils when of alkaline reaction.

The hydrogen ion concentration of the soils at the beginning and at the close of the experimental period was determined electrometrically by the use of the hydrogen electrode.

### EXPERIMENTAL DATA

STUDY OF CALCIUM CONCENTRATION
FIRST TRIAL

CALCIUM CONCENTRATION AND GROWTH OF ALFALFA - TABLE I

Series	Parts per million	Yield of tops
1	240	.297 Gm.
2	0	.064
3	2	.070
4	4	.082
5	8	.160
6	16	.180
7	32	.221
8	64	.214
9	128	.250
10	320	.273

The effect of different concentration of calcium did not become apparent in this trial until after the first week. The plants in series one made more growth than those in any other series. The plants growing in series two where no calcium was supplied had all died at the end of three weeks but a slight increase in length of roots was noticed. Plants growing in series three had all died at the end of three weeks also. Plants growing in four and eight parts per million died before the end of the period. Some growth of roots and tops took place. Nearly all the remaining plants growing in the solutions having a higher concentration of calcium lived the entire growth period extending from December 1, 1926 to January 12, 1927. The amount of top and root growth made was proportional to the calcium ion concentration of the nutrient solution up to 32 parts per million. Nodules were present on all the series except series 2, 3 and 4.

Dampening off fungus began to attack the experiment and at the end of six weeks it was brought to a close.

The observations made during the period of this trial leads one to think that the alfalfa plant must have a reasonable concentration of calcium in order that it may grow normally. Since most plants receiving 16 or more parts per million lived throughout the period, some indications of minimum concentration of calcium required is shown. Results are shown diagrammatically in Diagram I and they indicate that about 32 parts per million is the economic concentration of calcium for alfalfa for the conditions of this trial.

SECOND TRIAL

The second trial was carried on in the summer. It was similar to the first. The results obtained, follows:

CALCIUM CONCENTRATION AND GROWTH OF ALFALFA - TABLE II

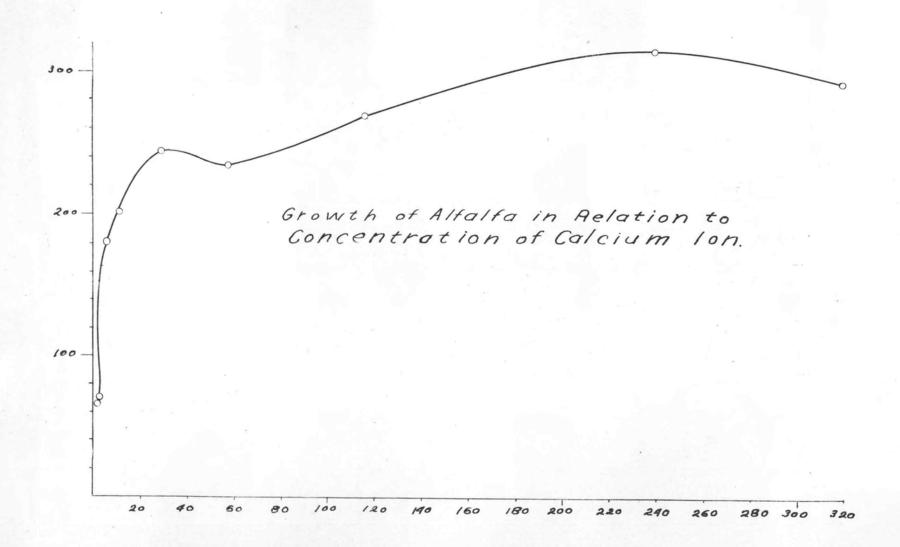
Series	Parts per million	Yield of tops	Yield of roots	Ratio tops to roots
1	240	.620 Gm.	.220 Gm.	1:33
2	0	.310	.070	1:23
3	Discontinue	d		
4	4	.350	.103	1:29
5	8	. 435	.109	1:25
6	16	.645	.211	1:33
7	32	.630	.273	1:43
8	64	.500	.192	1:38
9	128	1.265	.546	1:43
10	320	.995	.371	1:37

This experiment was carried on for six weeks or from May 18 to June 28, 1927.

During the first ten days of the experiment no difference in growth due to difference in concentration of the calcium ion was apparent.

The plants in the check series having 240 parts per million of calcium made satisfactory growth and developed normal sized leaves.

## DIAGRAM I



Nodules developed on the roots which were stubby and branching. These plants were not as tall as those in series containing 128 and 320 parts per million.

The plants in calcium free solution began to look chlorotic after two weeks. The edges of the leaves took on a reddish tinge which spread toward the midrib. No increase in leaf growth took place.

Some increase in root length was observed but there was no branching of roots. The roots became brownish in color about the time the leaves became chlorotic. Small nodules formed at first on the roots but these shriveled during the time that the plants were gradually dying.

The plants in series 4 having four parts per million of calcium lived the entire growth period, that is, there were one and two leaves alive at the close of the experiment on all the plants. The leaves died back and then a new one would come out, these forming in a whorl at the crown. The plant seemed to be making re-use of the limited amount of calcium available. The leaves were small and light green in color toward the close of the experiment. The roots were spindling with no root branches; however, a few root nodules were present.

The plants having 8 parts per million of calcium made slightly more growth than did those with 4 parts per million. The leaves were not normal in size but were darker green in color. The roots were more stocky with few branches and some nodules present. These roots were fully as healthy and stocky as those with 32 parts per million.

The plants in solutions containing 16 and 32 parts per

million of calcium made about equal growth. These plants were larger and healthier in color than those receiving 8 parts per million. The leaves of these plants appeared normal in size.

The plants receiving 64 parts per million of calcium developed better than the series having a lower calcium concentration during the first half of the trial; however, during the second half of the period, a black fungus attached the plants which retarded their growth considerably.

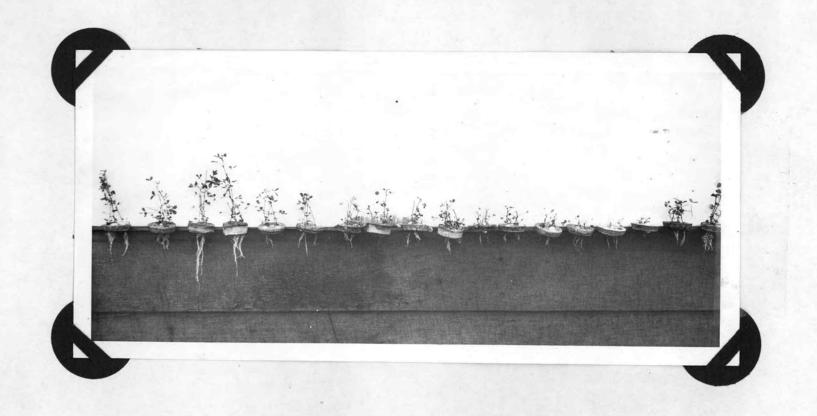
The plants receiving 128 parts per million of calcium made more growth than those in any of the other series. The tops grew to a greater height and had normal sized leaves. The roots were longer and had more branches than the plants in any other series. This series also had the greatest amount of nodules and was freer from insect injury than any of the other series.

The plants in series 10 having 320 parts per million of calcium did not make as much growth as those in series nine, probably due to a greater amount of insect injury by thrip and red spider. This series had a much more bushy root system than did series 9.

Photographs of representative plants taken at the time of harvest are shown in Figure 1. Effects of concentration is further shown in figure 2 from a previous trial conducted at this station (13).

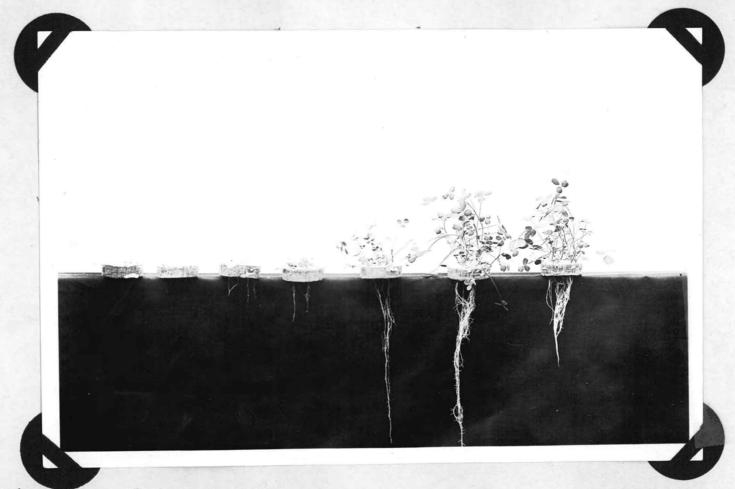
The entire experiment was sprayed several times to protect against thrip and red spider. These insects threatened injury at times throughout the period.

# FIGURE I



Calcium Concentration and Growth of Alfalfa P.P.M. 320 128 64 32 16 8 4 0 240

# FIGURE II



Calcium Concentration and Growth of Alfalfa P.P.M. 0 3 6 12 24 32 64

# CALCIUM IN THE SOIL SOLUTION AND AMOUNT OF REPLACEABLE CALCIUM EXPERIMENT I

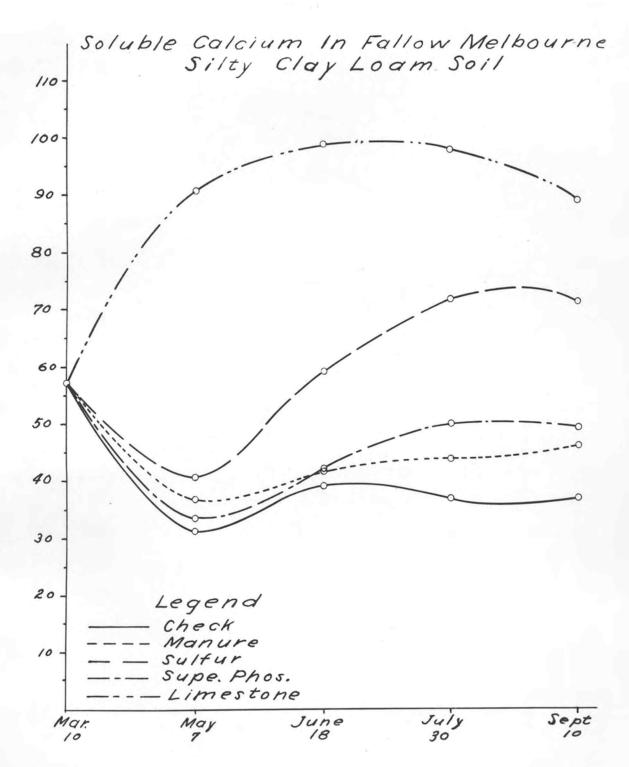
SOLUBLE AND REPLACEABLE CALCIUM IN CERTAIN FALLOW SOILS IN POTS TABLE III

Soil	:Treatment : per Acre		rt					of							Replace
		: :Ma	r	: 28:Ma	у	7:0	Tun	18:	Ју	30:	Sept	10:	Mar :	28:	Sept 10
	:	:		:		:		:		:		:		:	
Melbourne	:Check	:	57	:	31	:	39	:	37	:	37	:	265	3:	2915
11	:10 T	:		:		:		:		:		:		:	
	:Manure	:	57	:	37	:	42	:	50	) :	49	:	265	3:	3023
11	:250#	:		:		:		:		:		:		:	
	:Sulfur	:	57	:	41	:	59	:	72	:	71	:	265	3:	2881
11	:450#	:		:		:		:		:		:		:	
	:Sup Phos	:	57	:	33	:	39	:	43	3 :	46	:	265	3:	3286
11	:4 T Gr.	:				:		:		:		:		:	
	:Limestone	:	57	:	91	:	99	:	98	3 :	89	:	265	3 :	4015
Willamett	e: Check		42		22	:	33	3 :	47		60		2668	8:	2768
11	:10 T	:		:		:		:		:		:		:	
	:Manure	:	42	:	26	:	32	:	29	:	59	:	2668	8 :	3121
tt	:250#	:		:		:		:		:		:		:	
	:Sulfur	:	42	:	41	:	73	5 :	79	:	108	:	2668	8 :	2748
11	:450#	:				:		:				:		:	
	:Sup Phos	:	42		29	:	29	:	38	:	58		2668	3 :	2966
11	:4 T Gr.	:													
	:Limestone	:	42		96	:	76	:	72	:	93		2668	8 :	3206

An experiment using Melbourne Silty Clay Loam and Willamette Silty Clay Loam was started March 28, 1927. The fallow jars were kept at optimum moisture content. Samples were taken from the fallow jars periodically and water soluble calcium was determined. The replaceable calcium was determined on these samples at the beginning and at the close of the experimental period.

All the treatments on Melbourne Silty Clay Loam except limestone had a depressive effect upon the water soluble calcium content of the soil during the first six weeks as shown by Diagram 2. The calcium content had begun to increase again at the end of twelve weeks

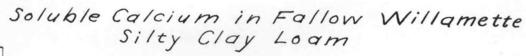
# DIAGRAM II

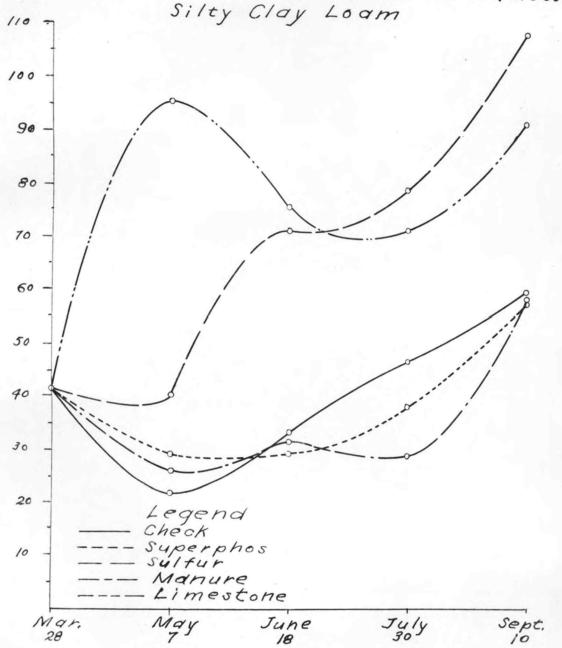


And continued to do so during the remainder of the experimental period. However, it had not exceeded the amount originally present. The amount of water soluble calcium increased rapidly until the maximum was reached at the end of twelve weeks in the limestone treated soil. The largest amount of water soluble calcium was present in the limestone treated soil at the end of the experiment. The sulfur treated soil contained the second largest amount, followed in turn by manure and super-phosphate. The largest amount of replaceable calcium was present in the limestone treated Melbourne soil at the close of the experiment, followed respectively by superphosphate, manure and sulfur. The amount present in the sulfur treated soil was smaller than that present in the check.

The effect of treatment on the water soluble calcium content of Willamette Silty Clay Loam was similar to the effect on Melbourne Silty Clay Loam as shown by Diagram 3. The application of manure and super-phosphate caused the water soluble calcium content to be less than that of the check during the latter half of the experimental period. The application of sulfur to this soil caused the amount of water soluble calcium to increase rapidly after the first six weeks. The amount of calcium present at the close of the experiment was larger where sulfur had been applied, than where limestone had been applied. This is in contradiction to the results obtained with the Melbourne Silty Clay Loam soil. Where limestone was applied, the amount of water soluble calcium reached its maximum during the first six weeks. It did not maintain this maximum but decreased during the next 12 weeks and then increased slightly to a point somewhat below its maximum. The

## DIAGRAM III





trend of the water soluble calcium content with respect to time of sampling is found in Diagram 3.

Willamette Silty Clay Loam soil treated with limestone contained the largest amount of replaceable calcium at the close of the experiment, followed respectively by the manure, super-phosphate and sulfur treated soils.

Two cuttings of alfalfa were obtained from the cropped series of jars. The yields are shown in the following table:

YIELDS OF ALFALFA OBTAINED ON UNTREATED AND TREATED JARS TABLE IV

	Treatment	First	Second	Total
Soil	per Acre	Cutting	Cutting	Yield
		Grams	Grams	Grams
Melbourne Silty C.L.	Check	2.4	3.0	5.4
	20,000# Manure	2.9	2.5	5.4
	250# Sulfur	1.7	2.3	4.0
	450# Super-phos.	3.7	3.1	6.8
	8000# Gr. Limeston	.e3.0	3.4	6.4
Willamette Silty C.L.	Check	3.5	1.4	4.9
	20,000# Manure	5.0	1.6	6.6
	250# Sulfur	4.0	1.9	5.9
	450# Super-phos.	3.5	1.8	5.3
	8000# Gr. Limestone	5.1	1.5	6.6

The yield of alfalfa was benefitted by the application of ground limestone which maintained a high concentration of the calcium ion in the soil solution throughout the period. However, the highest yield obtained on Melbourne soil was where super-phosphate had been applied. This might be expected since Melbourne Silty Clay Loam is a soil rather low in phosphorus content (1). On the Willamette soil, manure benefitted the growth measurably. The application of sulfur benefitted the growth of alfalfa on the Willamette soil and depressed the growth on the Melbourne soil.

EXPERIMENT II

# SOLUBLE AND REPLACEABLE CALCIUM IN CERTAIN FIELD SOILS TABLE V

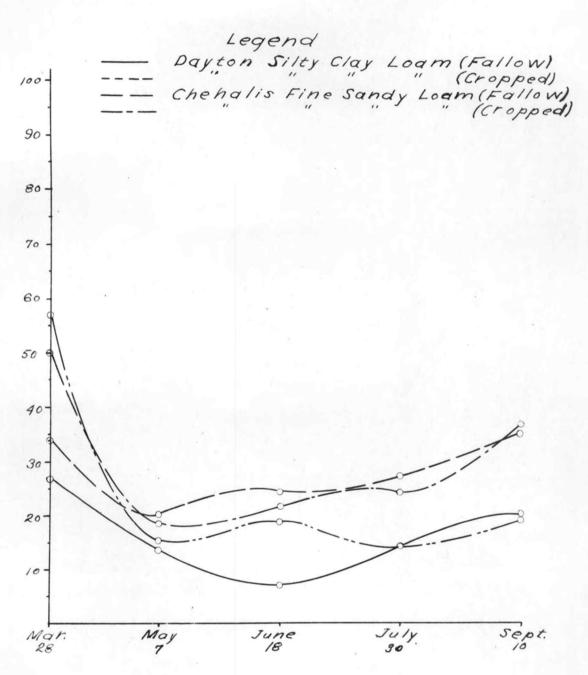
Soil	:Treatmen	t:	Par	ts	per	r M	il1:	ion	of	Wa	ter	: ]	P.P.M	·R	eplace-
	:	:			Sol	ubl	e Ca	alc	ium			::	able (	Ca	lcium
	:	:		:		:		:		:		:		:	
	:	: N	lar 2	8:1	My '	7 : J	n 18	3:J	y 29	9:S	ep 1	0:1	War 28	3:1	Sep 10
	:	:		:		:		:		:		:		:	
Dayton S.C.L.	:Fallow	:	57	:	15	:	18	:	14	:	19	:	2000	:	2081
11 11 11	:Cropped	:	27	:	13	:	7	:	14	:	20	:	1813	:	1948
Chehalis F.S.L	.: Fallow	:	34	:	20	:	24	:	27	:	35	:	2886	:	3157
11 11 11	:Cropped	:	50	:	18	:	22	:	24	:	37	:	3360	:	3551

This experiment was started March 28, 1927 and discontinued September 10, 1927. The effect of season and crop under field conditions upon the calcium content of soils was studied on Dayton Silty Clay Loam and Chehalis Fine Sandy Loam. Analysis for water soluble calcium was made at six week intervals. The amount of replaceable calcium present was determined at the beginning and at the end of the experimental period.

The relationship between the amount of water soluble calcium and the season in Field Soils is shown in Diagram 4. The amount of water soluble calcium present tends to decrease during the spring and early summer, due probably to solubility effect of increased moisture, to growing crop or chemical reactions which are brought about under the conditions present. There was a gradual increase during the summer and early fall due probably to increased biological activities. Similar results were obtained with the soils in the jars since they were subjected to outdoor conditions. The fallow soils contained somewhat more water soluble calcium than the cropped soils, during the entire period except at the time of taking the last sample. The Chehalis soil contained more water soluble calcium than the Dayton soil.

## DIAGRAM IV

## Soluble Calcium In Field Soils



CHANGE IN HYDROGEN-ION CONCENTRATION DUE TO TREATMENT IN FIELD AND POTS - TABLE VI

Soil	Treatment		ntration (pH) Sept. 10
Dayton S.C.L.	Fallow Cropped	5.47 5.47	5.44 5.46
Chehalis F.S.L.	Fallow Cropped	6.23	5.64 5.56
Melbourne S.C.L.	Check 10 T Manure 250# Sulfur 450# Super Phosphate 4 T Gr. Limestone	6.32 6.32 6.32 6.32 6.32	6.18 6.05 6.03 6.15 7.77
Willamette S.C.L.  " " "  " " "  " " "	Check 10 T Manure 250# Sulfur 450# Super Phosphate 4 T Gr. Limestone	6.57 6.57 6.57 6.57 6.57	5.78 5.78 5.44 5.64 7.26

ments 1 and 2 were determined at the beginning and at the close of the experimental period. The application of manure and sulfur had a positive effect on the hydrogen-ion concentration due probably to the acids formed in each case. Super-phosphate also had a positive effect on the hydrogen-ion concentration due possibly to the taking of calcium out of solution to form di-calcium phosphate. Since one of the main functions of calcium in the soil is to neutralize acidity, it was expected that the application of ground limestone would decrease the hydrogen ion concentration. One of the outstanding observations of the experiment is the apparent change in pH of the Willamette Silty Clay Loam soil during the period covered by this study, since it is a highly buffered soil and high in organic matter content.

#### DISCUSSION

The concentration of calcium ion required by the plant to make normal growth seems to be about 32 to 64 parts per million. This is in confirmation with the concentration indicated in a previous trial by Hartman (13). The plants were not injured by the higher concentrations employed, which would indicate that the calcium ion is not toxic when present in excess. Sixteen to thirty-two parts per million seems to be the minimum and thirty-two parts per million the most economical concentration. With higher concentrations, increased yields were obtained in accordance with the law of diminishing returns.

Dayton Silty Clay Loam, Chehalis Fine Sandy Loam, Willamette Silty Clay Loam and Melbourne Silty Clay Loam at certain seasons seems to be below that required by alfalfa to make normal growth. Stewart (36) found that the soil solution of some of the irrigated soils of California contained less calcium ion than that which seems to be the economic requirement of alfalfa in these experiments. Since the plant requires the largest amount of calcium during its early growth (5) it is important that the calcium content is maintained throughout the season (10).

If normal growth is to be maintained on certain soils, the application of limestone must be made at regular intervals. It is also possible to believe that a higher concentration of calcium is necessary in the soil solution than is required in a culture solution, since calcium performs many other functions in the soil, such as improvement of tilth, correction of acidity, aiding biological activity, aiding the

absorption of anione and neutralizing toxins. Furthermore, diffusion is probably slower in soils than in culture solutions.

The results reported here (Table III) tend to show that the production of acids in some soils seem to increase the water soluble calcium in proportion to the degree of ionization of the acid. The slightly ionized organic acids produced by the decomposition of manure did not bring as much calcium into solution as the highly ionized sulfuric acid in the two treated soil series.

Since many soils contain barely sufficient concentrations of calcium ions to supply the crop growing on them, and in view of the fact that some of that amount must be used for purposes other than nutrition, it is reasonable to believe that in order to obtain maximum yields of crops such as alfalfa and red clover, the application of lime is necessary from a nutritional standpoint as well as from the standpoint of the correction of soil acidity, improvement of physical condition of the soil and of biological acidity, improvement of physical condition of the soil and of biological activity. The amount of replaceable calcium present in the soil may represent a source of the water soluble calcium since it can be brought into solution by base exchange and by the action of acids formed within the soil. Analysis given in Table III show that the amount of calcium that disappeared from the replaceable form in the Melbourne soil is practically equivalent to the increase in calcium in the soil solution due to the treatment with sulfur. The lack of such relationship in the sulfur treated Willamette soil would indicate that a solubility effect had been experienced.

The results obtained in this study should be valued

conservatively since the period of time employed was rather short; also, in the study of the nutritional requirements no means of taking into account the amount of calcium present in the seed was employed. A continuance of the study of calcium concentration in the soil over a much longer period of time would yield results of greater value to a student of soil fertility.

- 1. This study concerns the concentration of calcium ion required by alfalfa in relation to the concentration of calcium present in the soil as water soluble and the amount on the ultraclay complex as affected by treatment, crop and season.
- 2. The following relationships were found between the alfalfa plant and calcium nutrition:
  - A. The minimum concentration of calcium required by the alfalfa plant to make growth appears to be 16 parts per million. The most economical growth was produced with about 16 to 32 parts per million.
  - B. Calcium ions present in excessive concentrations do not seem to be toxic to the plant, instead, increased growth may be produced.
  - C. The presence of sufficient calcium in solution produces a strong healthy plant with a stocky root system which when inoculated has a large number of nodules.
- 3. The studies of the effect of season and treatment on water soluble calcium content in soils, in field and in pots yield the following conclusions:
  - A. The water soluble calcium content of certain soils is found to be below the amount necessary for a satisfactory growth of alfalfa in solution culture.
  - B. The application of ground limestone and sulfur increases the water soluble calcium content of the

soils as used in this investigation.

- c. By the application of ground limestone, the water soluble content of some soils can be increased and maintained throughout the season at a concentration which will eliminate calcium as the limiting factor in plant growth.
- D. The soluble calcium content of some soils seems to be lowest during the early part of the season which is the time that the plant requires calcium in large amounts.
- 4. The amount of replaceable calcium present on the ultraclay complex varies during the season; also, the application of limestone tends to increase the amount present. It is probable that calcium tends to conserve the base absorbing capacity of the soil or prevent soil deterioration.
- 5. It is probable that the application of ground limestone to many soils would prove of benefit from a nutritional standpoint as well as from its physical, chemical and biological effects.

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