THE EFFECT OF SOIL CARBONATE ON THE AVAILABILITY OF ADDED AND NATIVE PHOSPHORUS IN SOME CALCAREOUS SOILS

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ABSTRACT

This investigation was initiated to investigate the effect of the carbonate content of the soil on the availability of recently added and native soil phosphate. The investigation included greenhouse and laboratory studies on four virgin and ten cultivated calcareous soils with a wide range of carbonate contents.

The results indicate that the carbonate content of a given soil is not a criterion of its phosphorus supplying power. Other factors including soil texture and previous management are shown to have an important influence on the availability of soil phosphate. Phosphorus added to the soils was readily available to the plants regardless of the CaCO3 content of the soil. A gradual reduction in the availability of added phosphate seems to take place. Highly significant positive correlations were obtained between the amounts of phosphorus taken up by the plants and the amounts of phosphorus extracted by either NaHCO3 or NH_hF extractants.

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I. INTRODUCTION

The phosphorus status of calcareous soils is usually attributed to reactions of slightly soluble calcium phosphates. In spite of conflicting findings, the conclusion that calcium carbonate depresses the solubility and the availability of soil phosphates to plants, is generally accepted. This conclusion is based on the effect of calcium carbonate on: the soil reaction, the reactive surface of the soil, and the source of calcium which is a common ion with calcium phosphate.

Relatively few investigations have been conducted on the effects of soil carbonate and its content on phosphate availability in calcareous soils. McGeorge and Breazeale (22), McGeorge (21), and Benne, et al.

(1) concluded that phosphate added to a medium containing calcium carbonate is converted to a more insoluble form. Gile and Ageton (15), Shreve and Wallory (32), Das (10), and Thorne (34) found that the addition of various amounts of calcium carbonate to the growth media depressed the growth of some plants, while growth of other plant species was hardly affected or was increased due to improved physical properties. Ridley and Hedlin (30) found a negative correlation between the calcium carbonate content of phosphate fertilized plots and sodium bicarbonate-extractable phosphorus. Fuller and McGeorge (13) found no correlation between carbon dioxide-extractable soil phosphorus and the calcium or "active" calcium content of the soil.

They concluded that phosphorus availability is influenced by other

factors as well.

Lewis, et al. (20), Olsen, et al. (26), Haddock and Linton (17), and Chumachenko (6) concluded that soluble phosphorus added to calcareous soils was available for a long period of time.

Since no conclusions could be drawn from previous findings, investigations were conducted to determine the effects of soil carbon-ate on the availability of added and native phosphorus in some calcareous Manitoba soils.

II. LITERATURE REVIEW

In 1914, Gile and Ageton (15) added varying amounts of calcium carbonate to a soil well supplied with nitrogen, potash, and phosphoric acid. They found that, although bush beans and radishes were unaffected in growth even by 35 per cent calcium carbonate, the growth of sunflowers, soybeans and sugar cane was somewhat depressed by 18 per cent calcium carbonate. The growth of sweet cassava was slightly depressed by 5 per cent calcium carbonate and remarkably so by 35 per cent. The growth of rice and pineapple was depressed by all three levels of calcium carbonate, and the plants were made chlorotic. Nitrogen, phosphorus, and potassium in the plants showed relationship to lime added to the soil. The total ash tended to increase and the iron in plants generally decreased as the lime content of the soil was raised. The calcium content increased in all of the plants studied except bush beans. They concluded that in general the plants least affected in growth by the lime treatments were also least changed in chemical composition.

In 1931, Shreve and Mallory (32) found that the growth of covilla was retarded by addition of increasing amounts of calcium carbonate to a naturally alkaline soil near Tucson, Arizona. The plants absorbed increasing amounts of calcium with each added increment of calcium carbonate to the soil.

Das (10) added variable amounts of chalk to a relatively fertile soil containing 14 per cent clay, 0.5 per cent lime, and having a

pH of 8.17. He found that chalk addition up to 30 per cent of soil weight increased the yield of Aleucina coracana. The increased yields were attributed to improved soil aeration from the chalk treatments. No chemical analyses were reported for the plants grown.

McGeorge and Ereazeale (22) conducted a series of experiments on calcareous Arizona soils. They concluded that the presence of calcium carbonate greatly reduces the solubility of phosphate in rock phosphate as well as in soils. They believed that upon addition of rock phosphate to a soil which contains an excess of calcium carbonate, the rock phosphate becomes saturated with calcium carbonate as an integral part of the molecule. This process leads to the formation of a very insoluble carbonato-apatite, the solubility of which is kept at a minimum by calcium ion activity in the soil solution and the carbonate ion concentration in equilibrium with the calcium carbonate solid phase.

They also found, using culture solution experiments in which wheat seedlings were grown for seven days, that the addition of calcium carbonate depressed the amount of available phosphate from dicalcium phosphate and tricalcium phosphate. They believed that both compounds combined with the calcium furnished by the calcium carbonate added.

On the other hand, they found that applications of superphosphate to calcareous Arizona soils notably increased the phosphate
concentration of the soil solution, and would maintain this increase
for a protracted period if good aeration and water penetration are

maintained. They concluded that the sclubility of phosphate from more soluble materials is less affected by calcium carbonate in soils.

In a later study on the availability of residual phosphate in Arizona soils McGeorge (21) concluded that soluble phosphates are fixed rapidly as tribasic calcium phosphate and that final conversion to calcium-carbonate-phosphate is a very slow process.

In 1936, Benne, Perkins, and King (1) studied the effect of pH on a system by using different reagents. They added various compounds of calcium, or a soil saturated with calcium, alone and in varying combinations, to portions of a standardized solution of 0.25 gm. of phosphoric acid (79.1 mgm. of phosphorus) diluted to 250 cc. They found that calcium ions did not precipitate phosphorus from solution until the pH approached 5.5. Maximum precipitation or minimum solubility was not reached until the pH approached 7.5. Large excesses of calcium carbonate failed to completely precipitate the phosphorus from solution. This was attributed to the slight solubility of the calcium carbonate. They also found that the soil saturated with calcium precipitated phosphorus similar to a sparingly soluble calcium salt of a weak acid. The phosphorus solubility curve of this soil was similar to that of calcium carbonate, but was displaced with respect to it, which they attributed to adsorption. The phosphorus solubility curve of the soil showed a minimum at pH 2.56, then a gradual rise occurred till a maximum was obtained at approximately pH 5. Additions of sodium hydroxide, calcium oxide, and calcium carbonate lowered the curve from the maximum at pH 5 but to different

extents and by slightly different paths. Calcium oxide caused complete precipitation of phosphorus at pH 7.46. Calcium carbonate did not raise the pH above neutrality and did not cause complete precipitation of the phosphorus. Sodium hydroxide raised the pH to 8, but complete precipitation did not occur.

Puri and Asghar (27) described a method for determining available phosphates in soils by carbon dioxide-saturated solution extraction. They concluded from their experimental data that the addition of calcium carbonate to the soil lowers the value for available phosphate as determined by this method.

In 1946, Thorne (34) used bentonite clay with a base exchange capacity of about 130 m.e./100 gm. to investigate the influence of calcium carbonate on the growth and composition of plants. Stone tomato and barley plants were grown in cultures consisting of calcium saturated bentonite clay mixed with sand, and varying amounts of calcium carbonate. The calcium carbonate/clay ratios in the cultures varied from 1/5-2/1.

Thorne found that the growth of stone tomato plants was some-what inversely proportional to the calcium carbonate concentration in the culture medium. The decreased growth was associated with increases in calcium and decreases in potassium and phosphorus concentrations in the plants.

In similar cultures, Velvon barley was decreased in growth by only the highest level of calcium carbonate employed (two parts calcium carbonate: one part clay). The chemical composition of barley was also much less affected by the calcium carbonate than was that of the tomato plants.

The growth and composition of tomato plants were also studied in other cultures in which three levels of calcium carbonate were mixed in combination with four different ratios of exchangeable sodium to calcium. Tomato growth decreased with increasing degrees of sodiumsaturation and the effects of sodium were accentuated by the presence of calcium carbonate. On the other hand, phosphorus content of the plants was increased by sodium and decreased by calcium carbonate.

Phosphorus uptake by the plants was closely related to water soluble phosphate in the culture media. Thorne concluded from the experimental data that in the alkaline range, pH is less important than such factors as exchangeable sodium and calcium carbonate in controlling phosphorus availability to plants.

In 1950, Fuller and McGeorge (13) evaluated the available phosphorus in twenty calcareous Arizona soils. They found a distinct relationship between the carbon dioxide-soluble phosphate and the phosphorus available to barley and tomato plants. They found that the calcium content of surface and subsurface soils fails to indicate that high values of carbon dioxide-soluble phosphate are necessarily correlated with low values of carbonate calcium or "active" calcium. Furthermore, a low ratio of "active" calcium to carbonate calcium was not always associated with high solubility of phosphorus though the ratio ranged from 0 to 6.8. "Active" calcium as distinguished from total carbonate calcium in this investigation represents the amount

of soil calcium that reacts with 0.2 N ammonium oxalate.

Data obtained by extracting soil samples with successive portions of water showed that only a small amount, from 22-38%, of the soluble phosphorus added to these calcareous soils is fixed in an insoluble form. Only this small amount appeared to have the characteristic of carbonato-apatite.

The conclusion that the phosphorus added to calcareous Arizona soils is not all fixed in a wholly insoluble form was supported by the field observations that the effects of phosphate fertilizers added to irrigated Arizona soils may influence crop production for many years after application.

In a later study Fuller and McGeorge (14) reported that in calcareous Arizona soils, unlike the surface soils, there appears to be a rather close relationship between carbon dioxide-soluble phosphate and "active" calcium within a single soil profile. There was a tendency for carbon dioxide-soluble phosphorus to decrease with greater depth. This decrease was associated with an increase in "active" and carbonate calcium. On the other hand, there was no correlation between "active" calcium and carbon dioxide-soluble phosphorus for the same depth among different soils. They concluded that different soils possess inherently different characteristics, making it improbable that a single threshold value for calcium for all soils below which there will be sufficient phosphorus for maximum plant growth, can be established readily. They believed that it is not unlikely that maximum calcium carbonate solubility is approached in the soil

solution of all these calcium dominated soils.

They concluded that phosphorus availability, however, is influenced not only by the calcium in the soil solution, but also by the nature and proportion of the different cations on the colloidal complex.

In 1950, Lewis, Baker, and Snyder (20) studied phosphorus fixation in irrigated Bannock loam, containing 6.1 per cent calcium carbonate, five pounds of P2O5 per acre of carbon dioxide-soluble phosphate and having a pH of 7.8. They reported that carbon dioxide-soluble phosphate data showed that when various types of phosphate carriers were added to this calcareous soil, a reduction in availability took place within 2h hours. When water-soluble fertilizers (treble and single superphosphate) were added, a fairly constant but slightly lower level was maintained throughout an incubation period of eight months. A 100-pound application of P2O5 per acre maintained a carbon dioxide-soluble phosphate level of 22-25 pounds of P2O5 per acre and a 50-pound per acre application maintained a level of 13-18 pounds per acre.

The same rate of applications of citrate-soluble fertilizers (precipitated and fused tricalcium phosphate) gave a level of 8-10 pounds of P_2O_5 per acre which was not significantly different from the level of the check.

Greenhouse yield data showed that the 100 pound per acre application of water-soluble fertilizers gave the highest yield followed by the 50 pound per acre application from the same fertilizers. Very

little, and non-significant, increases in plant growth over the check were obtained from the citrate-soluble fertilizer applications.

Three crops of Romaine lettuce utilized 24.6-44.3 per cent of the applied water-soluble phosphate.

Recently Olsen, et al. (26) used "A" values and four chemical extraction methods, Bray-, sodium bicarbonate-, water-, and carbon dioxide-extractable phosphorus, to evaluate the availability of residual phosphate in three calcareous soils from experimental plots which had received phosphate treatments under long-term crop rotations.

The calculated "A" values indicated that the relative efficiency of the phosphate residues compared to a freshly added resin phosphate (equal in availability to superphosphate) was:

- 26-30 per cent on Ft. Collins loam containing 2.3 per cent calcium carbonate
- 31-38 per cent on Pryor silty clay (manured plots) 1.1 per cent calcium carbonate
- 40-56 per cent on Tripp very fine sandy loam containing 0.22 per cent calcium carbonate.

They stated that the differences among the three soils in the relative efficiency of the phosphate residues could be affected by many factors, including calcium carbonate content, soil types, texture, and form of phosphate material added. Some evidence indicates that the initial level of available phosphorus is an important factor positively affecting the relative efficiency of the phosphate residues.

They also reported that soil type, texture, and calcium carbonate

content in the range from 0.2-2.3 per cent had little effect on the percentage recovery of the resin phosphate from the check plots when measured by the phosphorus uptake by the plants and the sodium bicarbonate-extractable phosphate. They found that when the initial level of available phosphorus was high, however, the percentage recovery was higher than at a low level of available phosphorus. The percentage recovery varied from 30-58 per cent of the added phosphorus.

They found that the Bray-, sodium bicarbonate-, and water chemical-extraction methods and surface phosphorus were highly correlated with "A" values. Phosphorus extracted by the carbon dioxide method gave the poorest correlation. All correlation coefficients were statistically significant.

Haddock and Linton (17) studied the response of peas to superphosphate and the relationship between sodium bicarbonate-extractable phosphorus and the yield and phosphorus content of peas. They carried on a five-year crop rotation experiment (potatoes-sugar beets-peas-2 years alfalfa) on a highly calcareous Millville loam of pH 8.0. One rate of superphosphate application of 44 pounds of phosphorus per acre was used.

They found that the yield of both pea vines and canning peas were increased significantly by the phosphate application. Yield response was in the order: current season application > 1 year residual (phosphorus applied to sugar beets) > 2 year residual (phosphorus applied to potatoes). In all three cases the yield was significantly higher than the checks. They estimated that the potato, sugar beet

and pea crops each remove approximately 10 pounds of phosphorus per acre. Taking this into consideration, they concluded that the crop utilization of available phosphorus can only partly explain the decreased responses from residual phosphorus. They believed that phosphorus fixation into an unavailable form must have taken place.

They also found significant correlations between the sodium carbonate-extractable soil phosphorus and the acid-soluble phosphorus in pea vines at four soil moisture conditions under sprinkler irrigation. All of the phosphorus in the current season application was extracted by the sodium bicarbonate method.

Ridley (30) found a negative correlation between calcium carbonate content and sodium bicarbonate-extractable phosphorus on plots ranging in calcium carbonate content between .32 and 6.96 per cent. These plots had received applications of phosphate over a long period of time. There was no such correlation on untreated plots.

Chumachenko (6) concluded from laboratory and laboratory-field investigations that phosphorus added to calcareous soils of Central Asia remains in a form available to plants for a long time.

III. MATERIALS AND METHODS

A. FIRST GREENHOUSE EXPERIMENT

Four soils taken from virgin sites were used in this experiment.

They have the following descriptions:

1. Isafold clay loam

Legal location: NW 5-18-4W

Soil survey map area: Teulon, Manitoba

Sub group: Calcareous Rego Black

Parent material: Very strongly calcareous glacial till

Drainage: Good

Topography: Very gently to gently sloping

Vegetation: Sedges, grasses and herbs

2. Balmoral heavy clay loam

Legal location: SC 19-15-3E

Soil survey map area: Teulon, Manitoba

Sub group: Calcareous Meadow

Parent material: Strongly calcareous, moderately fine to fine

textural deltaic sediments

Drainage: Poor

Topography: Smooth, level to depressional

Vegetation: Meadow grasses, reeds and sedges

3. Clarkleigh heavy clay loam

Legal location: NW 5-18-4W

Soil survey map area: Teulon, Manitoba

Sub group: Saline Meadow

Parent material: Thin deposit of lacustrine sediments over

strongly calcareous glacial till

Drainage: Poor

Topography: Depressional

Vegetation: Sedges, meadow grasses and herbs

4. Lakeland silty clay loam

Legal location: WC 23-16-2E

Soil survey map area: Teulon, Manitoba

Sub group: Calcareous Gleyed Black

Parent material: Strongly calcareous lacustrine sediments

Drainage: Imperfect

Topography: Level to very gently sloping

Vegetation: Aspen, willow, dogwood, rose and meadow grasses

and herbs

More detailed descriptions are outlined in Manitoba Soil Survey Soil Report No. 12 (29).

First Crop

The soils were sampled to the bottom of the A horizon. The samples were air dried, well mixed and ground to pass through 0.5 inch square sieve. A representative sample from each soil was taken and the following properties were determined: pH, the soluble salt content, moisture equivalent, carbonate content and the organic matter content. The procedures used for these determinations are described under analytical procedures. These data are summarized in Table I.

TABLE I

SOME CHARACTERISTICS OF THE SOIL SAMPLES
FIRST GREENHOUSE EXPERIMENT

: : Soil : :	CaCO3 %	organic matter %	pH	Conductivity milli mhos	Moisture equivalent
: Isafold	2.1	12.7	6.9	0.38	41.0
: Balmoral	8.3	13.2	: : 7.6	0.81	48.3
: Clarkleigh	14.0	7.7	7.9	1.6l;	41.2
: Lakeland	16.L	15.7	7.5	0.62	Ц 5. Ц
			•		:

The greenhouse experiment was set up to consist of these four soils with three treatments which were replicated four times. The treatments were as follows:

- I. Incubated with 100 p.p.m. of phosphorus mixed throughout. At seeding time phosphorus labelled with P32 was added at a rate equivalent to 48 pounds of P205 per acre.
- II. Incubated with no phosphorus added. At seeding time phosphorus labelled with P32 was added at a rate equivalent to 48 pounds of P_2O_5 per acre.
- III. Incubated with no phosphorus added.

The soil samples were divided into 4500-gram portions. For the soils receiving 100 p.p.m. of phosphorus, a stock solution aliquot containing .45 gm. of phosphorus as KH2PO4 was diluted to the volume required to bring the soil samples to their respective field capacities. Portions of the soil were placed in a glazed gallon pot, a small amount at a time, and sprayed with the phosphorus solution to insure as complete and uniform distribution as possible. The rest of the soil samples (treatments II and III) were placed in glazed gallon pots and watered to field capacity. All the pots were covered with polyethylene paper to prevent evaporation of moisture. The samples were incubated for four weeks in the greenhouse where the temperature was about 75°F.

At the end of the incubation period the samples were air dried and each treatment well mixed. A representative sample was taken from each treatment for determination of nitrate nitrogen and NaHCO $_3$ -

extractable phosphorus as described under analytical procedures.

The experiment was set up to consist of the three previously mentioned treatments. One replicate of each treatment consisted of 2000 grams of air-dried soil in an half gallon glazed pot. At seeding time, each replicate of treatments I and II were treated as follows: A one and a half inch layer of soil was removed. A 20 cc. aliquot of KH2POL solution containing 21 mgm. of phosphorus labelled with P32 to give about 400 µ curries/gm. of phosphorus was added in a circular band, then covered with a 0.5 inch layer of soil. P32 was in the form of $NaH_2PO_{\underline{l}_1}$ and was obtained from Charles E. Frosst and Co., Montreal. Twenty seeds of Parkland barley were evenly distributed and covered with the remaining soil. The check treatments were seeded in the same manner except that no phosphorus was added. All soils were watered to field capacity. Through weighing the pots every other day, enough water was added to maintain all pots at field capacity. pots were randomized on a greenhouse bench and rotated every week. The greenhouse was illuminated 16 hours a day and the temperature was around 75°F.

Two weeks after seeding, the treatments were thinned to 12 evenly distributed plants per pot. Nitrogen in the form of KNO₃ was added to bring all the soils to a level of 30 p.p.m. of nitrogen. Two weeks later, due to large plant growth, an additional 20 p.p.m. of nitrogen in the form of KNO₃ was added to insure that nitrogen would not be a limiting factor.

Six weeks after seeding, the plants in each pot were cut at

the soil surface and dried in an oven at 70°C. The oven-dried plant material from each pot was weighed, ground and wet ashed using the method developed by Jackson and associates (19). The radioactive phosphorus was determined in the samples from treatments I and II by the solution counting method. The total phosphorus was determined in all the samples using the Vanadomolybdophosphoric yellow color method (19).

Second Crop

After the first crop was harvested, the soil samples were kept in the greenhouse for six months in a dry state. The samples were then taken out of the pots and each treatment well mixed. The samples from treatment I and III were used to grow a second crop of barley without introducing any further treatments. For each soil, the samples from each treatment were divided into four replicates of 2000 grams of air-dried soil and placed in half gallon glazed pots.

The pots were seeded in the same manner described before.

Enough water was added to bring all the soils to field capacity.

Since the nitrate content of the soils was at a high level no additional nitrate was added.

The experiment was carried out under similar conditions as described for the first crop.

After six weeks the plants from each pot were cut at the soil surface, dried at 70°C., weighed, ground, wet ashed and the total phosphorus determined following the same procedures mentioned before.

B. SECOND GREENHOUSE EXPERIMENT

Ten cultivated surface soil samples (0-6") selected from three locations were used in this experiment. These three locations were:

1. Gnadenthal sandy loam (4 samples)*

Legal location: NE 33-1-3W

Soil survey map area: Winkler, Manitoba

Sub group: Rego Black

Parent material: Medium textured calcareous deltaic deposit

Drainage: Imperfectly to moderately well drained

Topography: Smooth, level to very gently sloping

2. Lakeland silty clay loam (3 samples)

Legal location: WC 23-16-2E

Soil survey map area: Teulon, Manitoba

This soil series is described under the first greenhouse experiment.

3. Lakeland clay loam (3 samples)

Legal location: SE 27-12-2E

Soil survey map area: Winnipeg, Manitoba

The same soil series as mentioned in 2.

The soil samples were air dried, each well mixed and ground to pass through a 0.5 inch square sieve. A representative sample from each soil was taken and the following determinations were conducted:

^{*}Unpublished information obtained from Manitoba Soil Survey, University of Manitoba.

texture, carbonate content and its particle size distribution, organic matter, pH, the soluble salt content, total phosphorus, organic phosphorus, and 1/3 atmosphere moisture content. Some of the characteristics of the soils are summarized in Table II.

The experiment consisted of four treatments which were replicated four times. One replicate of each treatment consisted of 1800 gm. of air-dried soil in a half gallon glazed pot. The treatments were as follows:

- I. Incubated with 40 p.p.m. of phosphorus mixed throughout.
- II. Incubated with 20 p.p.m. of phosphorus mixed throughout.
- III. Incubated with no phosphorus added. At seeding time 10 p.p.m. of P32 labelled phosphorus was added.
- IV. Check, incubated with no phosphorus added and carrier free P32 added at seeding time.

All the phosphorus added was in the form of KH2PO4. The phosphorus applied before incubation was added in the same manner described under the first greenhouse experiment. The incubation was carried out at field capacity for six weeks in the greenhouse where the temperature was around 75°F.

At the end of the incubation period the samples were air dried and each treatment well mixed. A representative sample was taken from each treatment and the following determinations were conducted.

- 1. Nitrate content.
- 2. Samples from the check, 20 p.p.m. and 40 p.p.m. treatments were analyzed for NaHCO3-extractable phosphorus.

TABLE II

SOME CHARACTERISTICS OF THE SOIL SAMPLES

SECOND GREENHOUSE EXPERIMENT

:Location:	CaCO3	0.M. %	pН	Conductivity milli mhos		P	Texture
: Altona							
: 1 :	o.55	: 7.9	7.3	1.24	774 :	455	S.C.L. :
2	0.53	4.7	7.7	0.82	677	406	S.L.
3	9.2	2.9	7.9	0.73	708	351	S.L.
: 4 :	10.2	3.8	7.9	0.87	777	408	S.L.
Teulon	:		· ;	•	*		· •
: 1	24.3	4.4	7.9	1.08	494	238	L,
2	27.9	6.2	7.8	1.81	641 :	356	L.
: 3	29.3	4.9	8.0	1.37	528 :	310	. I
7.72	;	: :		:	:	:	
:Winnipeg:	2.0	9,8	7.5	1.72	763 :	560 :	C.L. :
2:	14.6	9.6	7.8	2.57	915 :	634	. I. :
: 3 : :	33 .1	7.7	7.8	4.73	686 :	433	. I. :

3. The inorganic phosphorus content of samples from the check and 40 p.p.m. treatments was fractionated into aluminum, iron and calcium bound phosphate.

In the greenhouse each pot was seeded with 20 evenly distributed Garry oat seeds. Treatment III received 10 p.p.m. of labelled phosphorus in the same manner as described in the first greenhouse experiment. Nitrogen in the form of NH₄NO₃ was added to bring all the samples to the highest nitrate nitrogen content found after incubation. Potassium was added in the form of KCl to equalize the amount of potassium added in the 40 p.p.m. phosphorus treatment.

For the check samples carrier free P32 equal to the amount of P32 applied to the 10 p.p.m. treatment was added in solution of sufficient volume to bring the different soils to their respective field capacities. The rest of the samples were watered to the field capacity.

The pots were randomized in a greenhouse bed and rotated each week. Since this greenhouse experiment was carried out in May and June, no artificial illumination was applied. The pots were weighed every other day and enough water was added to maintain the soils at field capacity.

The plants were thinned to 12 plants per pot two weeks after seeding time. Two weeks later an additional 20 p.p.m. of nitrogen was added to all pots in the form of $NH_{\downarrow\downarrow}NO_3$ to insure that nitrogen would not be a limiting factor.

After 45 days the plants in each pot were cut at the soil

surface, dried at 70°C., weighed, ground, wet ashed, the radioactive phosphorus determined on the samples from treatments III and IV, and the total phosphorus determined on all the samples.

C. ANALYTICAL PROCEDURES

- 1. pH was determined in a soil-water saturation paste using a Universal-pH meter 22.
- 2. The soluble salt content. The soluble salt content was estimated by measuring the electrical conductivity of a soil-water saturation extract, using a conductivity bridge--model R. C. 16132.
- 3. Field capacity. For the first greenhouse experiment, this property was measured using the moisture equivalent procedure. In this procedure, the moisture held by the soil after centrifugation for 40 minutes at 2440 r.p.m. was determined and expressed as percentage of the oven-dry soil weight.

Since the soil samples used in the second greenhouse experiment were medium textured, it was thought more suitable to use the 1/3 at-mosphere procedure as outlined by the United States Department of Agriculture (37).

H. The carbonate content as $CaCO_3$. The method outlined by Ridley (30) was used. A two gm. sample of less than two mm. air-dry soil was digested in 60 ml. of 10% HCl for 10 minutes. The carbon dioxide evolved was sucked through a drying and absorption train consisting of concentrated H_2SO_4 , dehydrite and calcium chloride, then adsorbed by Ascarite in a Nesbitt tube. The air stream flowing through the apparatus was rendered free from CO_2 by bubbling it through

concentrated NaOH. The weight of ${\rm CO_2}$ absorbed by the Nesbitt tube was determined and expressed as percentage of ${\rm CaCO_3}$ equivalent.

- 5. Organic matter content. The procedure developed by Walkley and Black (40, 41) was used in which organic matter is oxidized by chromic acid.
- 6. <u>Nitrate determination</u>. The colorimetric nitrophenoldisulfonic acid method as modified by Harper (19) was used.
- 7. Total and organic soil phosphorus. The ignition method of Mattson, Williams and Barkoff as modified by Saunders and Williams (31) was used. In this method 2 gm. of air dry soil < 2 mm. was ignited in a silica crucible for one hour at 550°C. The ignited residue and a fresh 2 gm. lot of unignited soil were extracted overnight with 100 ml. of 0.2 N H₂SO_{l1} on an end-over-end shaker. Inorganic phosphorus was then determined by direct colorimetric estimation on the extracts. The difference between inorganic phosphorus from ignited soil (total phosphorus) and inorganic phosphorus from the unignited soil was taken as organic phosphorus in the soil.
- 8. <u>Texture</u>. The automatic pipette method used by Kilmer and Alexander as outlined by the United States Department of Agriculture (37) was used. The texture was obtained from a texture triangle chart (38).
- 9. Carbonate particle-size distribution. In the various soil fractions (sand, silt, and clay) obtained by the pipette method mentioned above the carbonate material was dissolved by 1 N sodium acetate buffered at pH 5, according to the procedure described by

- Jackson (18). The loss of weight after thorough washing was considered to be the carbonate material present in the particular fraction.

 Corrections were made for the weight of dispersing agent lost through washing.
- 10. Wet ashing of plant material. The plant material was oxidized by means of a ternary acid mixture HNO3-H2SO4-HClO4 (10-1-4) according to the procedure developed by Jackson and co-workers (19).
- ll. Radioactive phosphorus determination. The P32 was measured in the wet-ashed plant material using a solution counting tube.

 The beta-ray activity was measured by a Muclear-Chicago Model 161A basic Binary Scaler.
- 12. Total phosphorus content of plant tissue. The total phosphorus in the wet-ashed plant samples was determined colormetrically using the Vanadomolybdophosphoric yellow color method as outlined by Jackson (19).
- 13. 0.5 M NaHCO_3 -extractable phosphorus. The soil samples were analyzed for extractable phosphorus using 0.5 M NaHCO_3 at pH 8.5 according to the procedure described by Olsen, et al. (25).
- 14. Soil inorganic phosphorus fractionation. Inorganic phosphate was fractionated into aluminum, iron, and calcium phosphate according to the procedure developed by Chang and Jackson (5) as modified by Glenn, R. C., Hsu, P. H., Jackson, M. L., and Corey, R. B. (unpublished data). This was accomplished by using the various extraction procedures in the following order:
 - a. 0.5 N NHhF at pH 8.2 extractable phosphate which was

measured colormetrically by the Dickman and Bray method (11).

- b. 0.1 N NaOH-extractable phosphate which was measured colormetrically by the Truog and Meyer method (35).
- c. 0.5 N H₂SO_L-extractable phosphate which was measured colormetrically by the Truog and Meyer method.

Occluded phosphorus was not determined since the procedure was used to identify the forms of recently applied phosphorus.

IV. RESULTS AND DISCUSSION

A. FIRST GREENHOUSE EXPERIMENT

First Crop

The yield and per cent yield of barley are presented in Table The check treatment data reflect large differences in yield, being 4.6 and 9.7 gm. per pot for Clarkleigh and Isafold, respectively. However, these differences apparently were not related to the carbonate content of the soils as expressed as $CaCO_{3}$. This observation is clearly illustrated by the fact that there was no significant difference in yield between Isafold and Lakeland samples which had 2.1 and 16.4 per cent CaCO3, respectively. In spite of the abnormally large plant growth of the check treatments, phosphate treatments greatly increased the yield on all four soils. These increases, significant at the l per cent level, indicate that soil phosphorus supply was an important factor in limiting plant growth. It also suggests that the soil samples contained a high supply of nutrients other than phosphorus. phosphate treatments, there was no significant difference at the 5 per cent level between the yields from Isafold and Clarkleigh soils, which have 2.1 and 14 per cent CaCO3 respectively. In both treatments, Balmoral had the lowest barley yield, although this was not true of the check treatments. Statistical analyses of the data from all treatments showed no inverse correlation between yield or yield response and the carbonate content of the soil.

Phosphorus content of plant material (Table IV) gives further

TABLE III

YIELD AND PER CENT YIELD OF BARLEY (FIRST CROP)

; ;S	oil :	Ministrativa de la completa de la co	Yield gm./	pot	% yield (Gert. x 100)
: <u>:</u> /	Treatment:	III	: II	: I	ii II	: I :
**	Isafold :	9.7	: 13.8	14.4	:: :: 143.3 ::	: 148.5 :
4	Balmoral :	6.7	: 11.0	11.5	164.2	: 171.6 :
:	Clarkleigh :	4.6	: 13.0	15.2	282.6	330.4
:	Lakeland	8.6	11.9	13.4	138.4	155.8

Yield: L.S.D. between soils (P=0.05) 1.40 L.S.D. between soils (P=0.01) 1.72

L.S.D. between treatments (P=0.05) 1.21

L.S.D. between treatments (P=0.01) 1.49

The treatments were:

- I. Incubated with 100 p.p.m. of phosphorus and l_18 pounds per acre of P_2O_5 added at seeding time.
- II. Incubated with no phosphorus added, and 48 pounds per acre of P_2O_5 added at seeding time.
- III. Incubated with no phosphorus added.

support to the trends observed from yield data. With the exception of Clarkleigh, total phosphorus uptake from the check samples proved to be high compared with normal cultivated soils. The per cent phosphorus in the check treatment, however, was comparatively low in magnitude. This condition is further evidence that phosphorus was a limiting factor for plant growth in these soils. The significant response to added phosphorus is reflected by the large increase in total phosphorus uptake from treatments I and II. The high per cent phosphorus in treatment I would indicate a luxury consumption of this These observations are strong indications that large amounts of added phosphorus, both before incubation and at seeding time were available to the barley plants. In both phosphorus treatments, the total phosphorus uptake of barley from the Balmoral samples was the lowest of the four soils. Statistical analyses of the data indicate no significant correlation between either total phosphorus content or per cent phosphorus in plant material and CaCO3 content of the soil.

The availability of soil phosphorus and the phosphorus added before incubation was evaluated by the NaHCO3-extraction method and "A" values calculated according to Fried and Dean's equation (12).

"A" = Per cent plant phosphorus derived from the soil x rate of Per cent plant phosphorus derived from the fertilizer phosphorus applied

NaHCO3-extractable soil phosphorus from treatments I and III, percentage utilization of the labelled phosphorus, and "A" values calculated from treatments I and II are presented in Table V.

The data, from the NaHCO3-extractable phosphorus, indicate that

TABLE IV

PHOSPHORUS UPTAKE AND PER CENT PHOSPHORUS IN BARLEY PLANTS

(FIRST CROP)

Soil	Phosphorus uptake			4 :	Per cent phosphorus in plant material		
Treatment	III	; II	: :	::	III	; II	: I :
: Isafold	12.6	27.3	88.8	* * * * * * * * * * * * * * * * * * * *	0.130	0.198	0.617
Balmoral	12.1	. 22.7	: 51.7	::	0.181	0.206	0.450
: Clarkleigh	6 . 8	24.8	84.3	* * * * * * * * * * * * * * * * * * * *	0.148	0.191	0.555
Lakeland	12.6	24 . 4	: : 72.9 :	2 4 2 4 2 4	0.147	0.205	0.544

the Clarkleigh soil had the lowest amount of native available soil phosphorus, while the other soils had similar amounts. Phosphorus added before incubation greatly increased the NaHCO3-extractable soil phosphorus from each soil. If the amount of phosphorus that was extracted from the check treatment is subtracted from that extracted from treatment I, it is evident that this method extracted from 26-34 per cent of the added phosphorus. However, there was no apparent relationship between the amounts extracted and CaCO3 content. For instance, the smallest amount extracted (26 p.p.m.) was from the Balmoral soil which has 8.3 per cent CaCO3, while the highest amount (32.2 p.p.m.) was extracted from the Lakeland soil which contains 16.4 per cent CaCO3. Statistical analysis showed that a highly significant positive correlation existed between NaHCO3-extractable soil phosphorus and total phosphorus content of the barley plants from both treatments. The correlation coefficient was +0.937 which was significant at the 1 per cent level. At the same time no correlation between NaHCO3extractable soil phosphorus and CaCO3 level was detected.

In treatments I and II, per cent utilization of labelled phosphorus, listed in Table V, show abnormally high values for all soils. This indicates that phosphorus added in a band at seeding time was quite available to the barley plants regardless of the CaCO3 level of the soil. The percentage utilization of labelled phosphorus in treatment I was lower than the comparable values from treatment II. This could be attributed to the increase in available soil phosphorus due to the phosphorus applied before incubation.

TABLE V
"A" VALUES, PER CENT UTILIZATION OF ADDED PHOSPHORUS AND NaHCO3 -EXTRACTABLE PHOSPHORUS

()- • =	NaHCO3 ext	ractable P*	Treatmen	nt II	Treatment I	
Soil :	III p.p.m.	. I p.p.m.	% utilization of added P.	"A" values p.p.m.	% utilization of added P.	"A" value:
Isafold	20.0	: 54.0	51.1	3 3. 5	38.8	110.5
Balmoral	21.0	47.2	41.1	35.4	35.1	67.2
Clarkleigh :	14.4	42.0	50 . 5	29.1	43.3	97 . 3
Lakeland :	20.6	52.8	47.5	31.4	39 . 5	86.2

st After four weeks of incubation period

Fried and Dean (12) considered the "A" value for a particular soil to represent an amount of soil phosphate that is as available to plants as the phosphate added in a standard phosphate fertilizer. data tabulated in Table V indicate that there was a large increase in "A" values for treatment I as compared to values for treatment II. This observation substantiates that large amounts of the phosphorus added before incubation were as available to the barley plants as the labelled phosphorus added at seeding time. The differences between "A" values for treatments I and II, expressed in p.p.m. of phosphorus were 77.0, 68.2, and 54.8 for Isafold, Clarkleigh, and Lakeland soils, respectively, while Balmoral had the lowest value of 31.8. It is apparent that the availability of phosphorus after incubation was large and independent of the $CaCO_3$ level of the soils. A high correlation was found between the "A" values from treatment II and the total phosphorus uptake of barley from the check treatments. However, due to the small number of samples, this correlation was not significant. Meanwhile, a highly significant positive correlation was found between calculated "A" values for treatments I and II and corresponding NaHCO3-extractable phosphorus values. The correlation coefficient was +0.923 which was significant at the 1 per cent level. There was no significant correlation between $^{\mathrm{R}}\mathrm{A}^{\mathrm{H}}$ values and CaCO_3 content.

All the presented data indicate that the Clarkleigh soil was low in available soil phosphorus, and that phosphorus added to the Balmoral soil before incubation was comparatively less available than the phosphorus added to the other soils. However, both observations could not

be attributed to the CaCO3 content of the soil, since all the data were consistent in showing no apparent relationship between the availability of added or native soil phosphorus and the level of carbonate expressed as CaCO3 equivalent in the virgin soils used.

Second Crop

First crop data clearly indicate that large amounts of the phosphorus added before four weeks of incubation were available to barley plants. In order to investigate the availability of added phosphorus to following crops, and also whether incubation under field capacity was a factor in the high phosphorus availability to the first crop, the soil samples from treatments I and III were stored in a dry state for six months in the greenhouse. A second crop of barley was grown without introducing further treatments.

The results obtained are summarized in Table VI. It is noted that the second crop yield and phosphorus content of the plants were much lower than those of the first crop. This could be attributed to two factors: (a) breaking virgin soils into cultivation is usually accompanied by a temporary flush release of nutrients due to the fast decomposition of organic matter. Under field conditions, the large amount of nutrients released might lead to a declining luxury growth of the first few crops. However, under greenhouse conditions, where nutrient consumption is relatively higher, the effect of the released nutrients might be confined to the first crop; (b) the high amounts of phosphorus utilized by the first crop.

However, the data indicate that, on all four soils, large and

TABLE VI

YIELD, PER CENT YIELD, PHOSPHORUS UPTAKE AND PER CENT PHOSPHORUS IN BARLEY (SECOND CROP)

Soil	Yield gm./pot		% yield Fert. x 100	ā "	rus uptake /pot	% P. in plant material	
8 9 9	III	I	CK 100	III	Ι	III	Ţ
: Isafold	2.14	3.80	177.6	2.89	10.19	0.135	0.268:
: Balmoral	2.78	3.34	120.1	4.72	11.42	0.170	0.342:
: Clarkleigh	2.50	3.48	139.2	3.74	11.8	0.150	: 0.339 :
: Lakeland	1.80	3.19	177.2	2,52	11.11	0.140	0.348 :

Yield: L.S.D. between treatments (P=0.05) 0.54 L.S.D. between treatments (P=0.01) 0.73

L.S.D. between soils (P=0.05) 0.76

Phosphorus uptake: L.S.D. between treatments (P=0.01) 0.69

L.S.D. between soils (P=0.01) 0.97

significant increases in yield and phosphorus content of the plants were obtained from treatment I samples. It is noted that per cent phosphorus in the plants from the check treatment were low and similar to the comparable values for the first crop. Per cent phosphorus in the plants from treatment I was significantly higher and comparable to values normally obtained from cultivated soils well supplied with phosphorus. This observation suggests that other factors were limiting the plant growth on treatment I samples. Previous observations illustrate that in spite of storing the soil samples in a dry state for six months, the incubated phosphorus had a considerable residual effect on the second barley crop. Data show that in both treatments, the CaCO₃ content of the samples had no apparent influence on residual phosphorus availability to the second crop of barley.

B. SECOND GREENHOUSE EXPERIMENT

The results presented in the first part of this investigation led to the conclusion that the availability of added and native phosphate in the four virgin calcareous soils was not related to the CaCO3 content. In order to investigate the effect of different levels of CaCO3 on phosphorus availability in cultivated soils, a second greenhouse experiment was carried out. Ten soil samples which ranged in CaCO3 content from 0.5 to 33.1 per cent were used in this experiment. These samples were collected from three locations. Thus for samples from the same location similarities in soil type, parent materials and previous treatments would be secured. At each location it was noticed that the CaCO3 content of the surface soil was quite variable.

These differences could be attributed to many factors, including variability in local mixing with lower soil horizons richer in CaCO3 content, thickness of the A horizons, and topography.

Since surface reactions are generally considered to be an important factor in the effect of CaCO₃ on phosphorus availability, the particle size distribution of the carbonate materials in the soil samples was determined. The results obtained are tabulated in Table XIV (Page 57).

The experiment was designed to consist of four treatments. In two treatments, phosphorus was applied at the rate of 20 and 40 p.p.m. of P. before incubation. Two rates were used in this experiment to investigate the relationship between the rate of phosphorus application and the CaCO3 effect on phosphorus availability. In a third phosphorus treatment, phosphorus labelled with P32 was applied at a rate of 10 p.p.m. at seeding time. The available soil phosphate would be estimated from this treatment according to Fried and Dean's formula (12).

Fried and Dean's method was criticized by Sokolov (33) who believed that the application of a phosphate fertilizer changes the composition and properties of phosphates already in the soil. Thus with different forms, dates, and methods of labelled fertilizer application, different estimates of available soil phosphates would be obtained. He suggested the application of labelled phosphate containing only a negligible amount of total phosphorus which would exert almost no effect on the composition or availability of soil

phosphates. In this method the stipulated store of available phosphates in the soil ${}^{tt}X^{tt}$ is determined by the formula:-

"X" = Amount of phosphorus taken into the plant x 100 K (utilization coefficient of P32)

He stated that this evaluation is based on the proposition that the P32 is distributed among different forms of the soil phosphates in proportion to their participation in the process of transferring phosphorus from the solid phase into the soil solution and vice versa. He believed that the method proposed makes it possible, through determination of a P32 utilization coefficient, to characterize the supply of exchangeable phosphates in the soil and the degree of their mobility, or in other words, their contribution to phosphate in soil solution which is available to plants. Sokolov's method was applied in this experiment. Carrier free P32 was added to the fourth and check treatment to determine Sokolov's "X" values and P32 utilization coefficients for the different soil samples.

Oat plants were used in this experiment since these plants are less susceptible than barley to powder mildew which was abundant in the greenhouse at the time of the experiment.

Yield of oats and per cent yield data are presented in Table VII. The data indicate considerable differences among the check yields from different soil samples. If the check yields from samples of the same location are compared as a separate group, it is noted in the Altona and Winnipeg locations, where there are wide ranges in CaCO3 content, that there is evidence of an inverse correlation between the CaCO3 contents of

YIELD AND PER CENT YIELD OF OATS

Soil	Yield (oven dry weight) gm./pot				### ### ### ### ### ### ### ### #### ####			
Treatment	Che c k	10 p.p.m. (band)	20 : p.p.m. :	: 40 : р.р.т.		10 ; p.p.m. ; (band) ;	20 p.p.m.	: 40 : : p.p.m. :
Altona :	5 .2 7	5.60	6.03	6.16	200	106.3	114.4	116.9
2	3.68	5.06	5 .5 0	5.42	* *	137.5	149.5	147.3
3	2.47	4.00	4.08	5 . 08	::	161.0	165.2	205.7
<u> </u>	2.96	4.16	5.14	5.54	::	140.5	173.6	187.2
Teulon : 1 : 2 : 3	5.41 5.85 5.08	5.98 6.18 6.06	5.99 5.89 5.87	6.82 6.09		110.5	110.7	126.1 104.1
: Winnipeg : 1 : 2	5.28 4.15	5.57 5.62	6.35 : 6.35	6.98 6.29		105.5	120.3	: 132.2 : 151.6 :
: 3 : : :	2.94	4.87	4.54	6.07	::	165.6	154.4	206.5

Yield: L.S.D. between treatments (P=0.05) 0.24 L.S.D. between treatments (P=0.01) 0.28

L.S.D. between soils (P=0.05) 0.38 L.S.D. between soils (P=0.01) 0.44

the Teulon samples are uniformally high, the check yields were high and comparable to those from the samples with low CaCO₃ content. If the check yields from all the samples are compared, no significant inverse correlation between the CaCO₃ content and the yield magnitude is obtained. This is illustrated by the following observations:

(a) Teulon 2 sample had the highest check yield although it contains 27.9 per cent CaCO₃; (b) there are no significant differences between the check yields from Altona 1, Winnipeg 1, Teulon 1 and 3 samples, in spite of the fact that they contain 0.5, 2.0, 24.3, and 29.3 per cent CaCO₃ respectively; (c) there is a significant difference at the 1 per cent level between the check yield from Altona 1 and 2 samples although they have similar CaCO₃ contents.

With the exception of one yield value (Teulon 2 sample treated with phosphorus at a rate of 20 p.p.m. of P.) there was significant yield responses from all the samples to each phosphorus treatment. In general the lower was the check yield, the greater was the response to phosphorus treatments. This is illustrated by the fact that although the check yields from Altona 1, Teulon 3, Winnipeg 2 and 3 samples range from 2.94 to 5.27 gm./pot, there are no significant differences among the 40 p.p.m. treatment yields from these soils. This indicates that phosphorus was an important growth limiting factor in these soils.

The low yield responses to phosphorus treatments on Teulon samples indicate that a high CaCO3 content is not necessarily associated with high yield response to phosphorus treatments.

In general, statistical analyses of the data indicated that in

all four treatments, there was no significant inverse correlation between either yield or per cent yield and the ${\rm CaCO}_3$ content of the samples.

Phosphorus uptake and per cent phosphorus in the oat plants (Table VIII) indicate similar trends to those observed from the yield data. In the check treatment, phosphorus uptake from different samples was quite different, reflecting large differences in available soil phosphorus among the different samples. If phosphorus uptake values from the check treatment samples of the same location are compared separately, it is noted in the Altona and Winnipeg locations, that there is an inverse relationship between CaCO₃ content and phosphorus uptake. However, phosphorus uptake from Teulon check samples was comparatively high and comparable to phosphorus uptake from the samples of low CaCO₃ from the other two locations.

Each phosphorus treatment significantly increased phosphorus uptake from all samples. With very few exceptions the higher was the rate of added phosphorus the higher was the increase in phosphorus uptake. In each phosphorus treatment, the increase in phosphorus uptake from the different samples had no apparent relationship with the CaCO₃ content. This is clearly illustrated by per cent utilization of added phosphorus in the three phosphorus treatments (Table IX). Per cent utilization of added phosphorus in the 10 p.p.m. treatment, which was labelled with P32, was obtained by measuring P32 uptake by the oat plants. Per cent utilizations of added phosphorus in the 20 and 40 p.p.m. treatments were obtained by expressing the increase in phosphorus uptake, due to each phosphorus treatment, as per cent of

PHOSPHORUS UPTAKE AND PER CENT PHOSPHORUS IN OAT PLANTS

: : : Soil		Phosphorus uptake mgm./pot				Per cent phosphorus in plant material			in
•	Check	10 p.p.m.	20 p.p.m.	p.p.m.	• • •	Check	10 p.p.m.	20 p.p.m.	140 p.p.m.
: Altona : 1	: 10.4	: : 12.8	16.6	18.3	: :	0.197	: : 0.229	: : .275	: : .297
2	6.9	9.4	11.9	12.9	::	0.188	: : 0.186	: : .216	: • •238
3	4.4	6.6	9.1	: 11.7	::	0.178	: : 0.165	: : .223	: .230
<u>L</u> ‡	3.0	7.5	10.3	11.4	::	0.101	. 0.180	. 200	.206
Teulon	: :	;	; ;	· •	::			•	•
1	: 7.3 :	10.1	13.0	: 16.5	::	.1 35	0.169	.217	. 242
2	9.8	12.3	13.6	16.2	::	0.168	0.199	.231	.267
3	7.2	10.6	11.0	15.7	• • • • • • • • • • • • • • • • • • • •	0.142	0.175	.187	.239
Winnipeg	: : :		;		::	3			
1	8.5	10.9	14.0	16.3	::	0.161	0.196	.220	.234
2	5.5	9.8	9.4	12.9	::	0.133	0.174	.190	. 205
3	2.0	8 . 6 :	8.9	12.8	::	0.068	0.177	.196	.211

Phosphorus uptake: L.S.D. between treatments (P=0.05) 0.41 L.S.D. between treatments (P=0.01) 0.48

L.S.D. between soils (P=0.05) 0.65 L.S.D. between soils (P=0.01) 0.76

Per cent phosphorus: L.S.D. between treatments (P=0.05) 0.008 L.S.D. between treatments (P=0.01) 0.009

L.S.D. between soils (P=0.05) 0.0125 L.S.D. between soils (P=0.01) 0.0145

TABLE IX

PER CENT UTILIZATION OF ADDED PHOSPHORUS

Soil	<i></i>		2 0
	: 10 p.p.m.	20 p.p.m.	; 40 p.p.m.
Treatm	ient:		
: Altona	:		: :
1	22.5	17.5	: 11.1 :
: 2	30.7	14.1	: 8.5
3	29.2	13.3	: 10.3 :
14	: 26.6	: 20 . 6	: 11.9
:	;	:	:
: Teulon	: 20.9	16.1	: : 13.0
: : 2	: 18.7	10.7	9.0
; 3	: 23.9	10.7	12.0
:			
: Winnipeg		:	:
: 1	: 23.3 :	15.5	: 11.0 :
: 2	21.4	11.0	10.5
: 3	24.0	19.4	15.3
		and the state of t	

the added phosphorus. It is apparent in each treatment that per cent utilization of added phosphorus was independent of the CaCO₃ content of the sample. In other words, the CaCO₃ level in the samples apparently did not affect the availability of added phosphorus in all three treatments.

Data presented in Table VIII indicate that in the check treatments there is an inverse correlation between the per cent phosphorus in the plants and the per cent CaCO3 in the soil samples. This correlation had a "r" value of -0.61 which was not significant at either the 1 or 5 per cent level. This is the first indication in the investigation that CaCO3 per se had any affect on the phosphate supplying power of the soil.

With the exception of two values, each phosphorus treatment significantly increased the per cent phosphorus in the oat plants. The higher was the rate of added phosphorus, the higher was the increase in per cent phosphorus. In each phosphorus treatment the increase in per cent phosphorus for the different samples was independent of the CaCO3 content.

Statistical analyses indicated that in all phosphorus treatments, per cent phosphorus in plant materials had no significant correlation with the CaCO3 content of the soil samples.

Available soil phosphate was estimated by two methods; "A" values calculated according to Fried and Dean's formula (12), and estimating soil exchangeable phosphate with P32 and its utilization coefficient as proposed by Sokolov (33). The data obtained from these

methods are tabulated in Table X.

The "A" values indicate large differences in available soil phosphate among the soil samples. It is noted that Altona 2, 3, and la samples which had the lowest "A" values are also the lightest in texture and contain some of the lowest levels of organic matter among the samples under investigation. This might be an indication that available soil phosphate has some relationship with either soil texture or organic matter content, or both of them. There was no significant correlation between the CaCO3 content of the samples and the available soil phosphate estimated by the "A" values. Meanwhile there was a highly significant positive correlation between "A" values and phosphorus uptake from the check treatment soil samples. The correlation coefficient was 0.834 which was significant at the 1 per cent level.

The values of exchangeable soil phosphate, "X", and its utilization coefficient (Table X) should be considered cautiously due to the fact that carrier free P32 was found to be adsorbed on the glassware. Carrier free P32 was applied to the soil samples in the form of a water solution. Part of this solution was kept as a standard, the activity of which could be determined at the time of the P32 estimation in the plant material. Thus per cent utilization of the added carrier free P32 could be calculated by relating the amounts of P32 to parallel standard counts. However, it was found that large amounts of P32 from the standard solution had been adsorbed on the glass container. This resulted in lower standard counts than there should have been. Since both the carrier free and 10 p.p.m. treatment

standards contained identical amounts of P32, and since negligable amounts of P32 adsorption occurred in the latter standard, P32 counts from the 10 p.p.m. treatment standard were used in calculating the carrier free P32 utilization coefficients and exchangeable soil phosphate of the different samples. This modification was done on the assumption that the amount of P32 adsorbed from the carrier free standard, at the time of application of the soil samples, was comparatively small relative to P32 in solution.

Nevertheless, since carrier free P32 was added to the soils within a short period of time, it is reasonable to assume that the amounts of P32 added to the different samples were equal. Thus the data obtained could be useful in comparing the availability of soil phosphate among the soil samples.

The amounts of exchangeable soil phosphates, measured by the "X" values, differed greatly among the different samples. However, these values were not related to CaCO3 content of the samples. Meanwhile there was a significant positive correlation between "X" values and per cent clay in the samples. The correlation coefficient was 0.744 which was significant at the 5 per cent level. A higher positive correlation was obtained between "X" values and per cent clay in the samples after removal of the carbonate materials from the clay fractions (Table XI). The correlation coefficient was 0.775 which was significant at the 1 per cent level. This indicates that exchangeable soil phosphates measured by this method were related to the mineral clay content of the samples.

TABLE X
"A" VALUES, "X" VALUES, AND CARRIER FREE P32 UTILIZATION COEFFICIENTS

Soil	: "A" values p.p.m.	Carrier free P32 utilization coefficient %	Sokolov "X" values p.p.m.
: Altona : 1	: : : 24.5	7.07	82.7
: 2	7.7	9.56	41.0
: : 3	5.7	: 5.04	42.3
: : :	: 2.5 :	14.014	; hh • 0 ;
Teulon	: : 16.9	6.06	73.7
: : 2	26.5	5. 03	103.0
: : 3 :	: : 14.7	7.68	52.2 :
Winnipeg	: : : 16.5	: : : 4.01	: 119.5
: 2	: 15.2	: : 3.51	87.6
: : 3 :	9.8	3.41	34.0

TABLE XI SAND, SILT, AND CLAY FRACTIONS BEFORE AND AFTER THE REMOVAL OF ${\tt CaCO}_3$

Soil		Before the rem oval of CaCO3			:: After the :: removal of CaCO3			
Treatment	Sand %	Silt %	Clay %	::	Sand %	Silt %	Clay %	
: Altona :	58 . 3	15.3	26.4	::	58 . 3	: 14.5	26.4	
2	71.3	11.5	17.2	* * *	70.0	: 11.5	17.2	
3	74.7	11.8	13.5	::	73.8	: 1.7	10.3	
14	70.6	10.3	19.1	::	70.6	8.9	11.5	
: Teulon :	40.2	37.6	22.2	***	37.4	: : 24.0	10.1	
2	46.5	34.9	18.6	::	42.7	: 1.9	17.4	
: : 3 :	44.3	36 . 4	19.3	::	40.1	: 12.9 :	10.2	
: Winnipeg : 1	28.7	35 . 8	35.5		28.2	: 32.6	: : 35.5	
: 2 :	28 . 5	46.2	25.3	::	26.1	: 31.7	24.3	
; ; ; ; ; ; ; ; ; ; ; ; ; ; ; ; ; ; ;	33.9	45.4	20.7	::	28.5	: 13.4 :	11.8	

It is apparent from the data that some of the samples (Altona 2, 3, and 4 samples) had similar amounts of exchangeable soil phosphates, yet their utilization coefficients were different. The comparable data from Altona 1 and Winnipeg 2 samples showed the same trend. This suggests that in different soils, soil phosphates exchangeable with P32 are not equally available to plants. This conclusion is in agreement with the results obtained by Kortiskaya*. This conclusion could explain the fact that the positive correlation between phosphorus uptake by the oat plants and the exchangeable soil phosphates in the different samples (0.717) was lower than the comparable correlation with "A" values (0.834). However, exchangeable soil phosphates determination seems to give a more comprehensive picture of the soil phosphorus potential supply.

The NaHCO3-extraction procedure developed by Olsen, et al. (25) was used to evaluate the availability of added and soil phosphate of the samples used in the second greenhouse experiment. NaHCO3-extractable phosphorus from the check, 20, and 40 p.p.m. treatments before seeding and after harvesting the oat crop are reported in Table XII.

Before seeding, NaHCO3-extractable phosphorus from the different samples was not necessarily related to CaCO3 content. If the extractable phosphorus from samples of the same location are compared, it is noted that the samples with the highest amount of extractable phosphorus are also the heaviest in texture and the highest in organic matter

^{*} These results are referred to by Sokolov, A. V. (33).

content. Statistical analyses showed a positive correlation between NaHCO3-extractable phosphorus from the check samples and the mineral clay content of the samples. The correlation coefficient was 0.633 which was significant at the 5 per cent level. Meanwhile, there was a positive correlation between organic matter content of the samples and NaHCO3-extractable phosphorus from the check samples. However, this correlation (r=0.545) was not significant at the 1 or 5 per cent level.

Both phosphorus treatments considerably increased the amounts of NaHCO3-extractable phosphorus from all the samples. If the increase in extractable phosphorus from each soil is related on a per cent basis to the rate of added phosphorus it is noted that 42.0 to 64.5 per cent and 55.0 to 62.0 per cent of the added phosphorus in the 20 and 40 p.p.m. treatments respectively were extractable by the NaHCO3 extraction. This indicates that, regardless of CaCO3 content, large proportions of the phosphorus mixed throughout the samples and incubated for four weeks were extractable by the NaHCO3 method. Statistical analyses indicated that phosphorus uptake by the oat plants was positively correlated with NaHCO3-extractable phosphorus before seeding time in all three treatments. The correlation coefficient was 0.892 significant at the 1 per cent level.

At the end of the greenhouse experiment, a reduction in NaHCO3-extractable phosphorus was clearly noticeable in all cases. Since this reduction could not be accounted for entirely by the amounts removed by the oat plants, this would indicate that during the crop

TABLE XII

NaHCO3-EXTRACTABLE PHOSPHORUS

Soil	*	Before seed p.p.m.	ding	At the end of the experiment p.p.m.			
*	: Check	20 p.p.m.	40 p.p.m.	:: Check	20 p.p.m.	40 p.p.m.	
: Altona : 1	: : 25.0	38 . 9	51.0	:: :: 21.8	26 . l4	42.3	
2	9.5	19.7	: : 33 . 6	6.4	12.5	25 . 9	
: 3	7.0	19.2	30.0	:: 6.0	10.j	22.6	
: 4	6.8	17.8	30.0	:: 6.0	9.8	21.3	
Teulon	14.0	26,9	1,2.8	:: 10.1	16,3	26.9	
2	: 17.0 :	30.7	43.0	:: 15.4	18.7	31.7:	
: 3	13.0	23.5	39.6	:: 10.1	15.0	23.8	
: Winnipeg	18.0	26.Lı	40.0	:: 15.8	18.3	31.2	
2	11.5	20.6	37.8	:: 10.1	14.6	25.0	
3	10.0	18.7	33.5	7.3	11.2	24.0	

growing period some of the added and native soil phosphate were converted to less available or unextractable forms. With few exceptions the reductions in NaHCO3-extractable phosphorus from the samples receiving 20 and 40 p.p.m. of P. were generally uniform and within the same order of magnitude for both treatments. This indicates that the reduction in NaHCO3-extractable phosphorus was independent of the rate of phosphorus application. However, the reductions in NaHCO3-extractable phosphorus in the phosphorus treated samples were considerably higher than comparable reductions in the check samples. This suggests that during the growing of a crop there is a gradual conversion of added phosphorus to a less available form in these soils.

In all three treatments, the reduction in NaHCO3-extractable phosphorus was not related to CaCO3 content of the samples. This indicates that the CaCO3 content had no apparent effect on phosphate conversion to less available or unextractable forms.

Statistical analyses of the data presented in Table XI showed no significant correlation between NaHCO3-extractable phosphorus and the CaCO_3 content of the soil samples.

The modified Chang and Jackson's fractionation procedure of soil inorganic phosphates was used to investigate the effect of CaCO3 content on the type and the relative availability of the different chemical forms of soil and recently added phosphates.

The soil samples were extracted by three reagents in the following order, 0.5 N NH_LF, 0.1 N NaOH, and 0.5 N H₂SO_{μ}. These reagents are considered to extract aluminum bound, iron bound, and calcium bound

phosphates respectively. The significance of these terms will be elaborated on in the general discussion.

The extracted phosphate fractions of soils which were sampled before seeding time and at the end of the greenhouse experiment are reported in Table XIII. The iron bound phosphate fraction was not reported since only trace amounts were detected.

The analyses before seeding time show that in all the soil samples under investigation, most of the extracted soil inorganic phosphates were in a calcium bound form. The rest of the extractable phosphates were recovered in the NH,F extract. The amounts of phosphorus extracted by either reagents were not necessarily related to the CaCO3 content of the samples. There was a positive correlation between the NH,F-extractable phosphorus and the mineral clay content of the samples. However, the correlation coefficient (+0.577) was not significant at either the 1 or 5 per cent levels. Meanwhile, the NH), F-extractable soil phosphorus was highly correlated with the exchangeable soil phosphates estimated by Sokolov's method (33). The correlation coefficient was +0.801 which was significant at the 1 per cent level. This, coupled with Weir and Soper's finding (42) that a high percentage of the NH1 F-extractable phosphorus was readily exchangeable with P32 in solution, shows that the NHLF-extractable phosphate form is a labile one.

Within experimental error, all the added phosphorus in the 40 p.p.m. treatment was recovered by the fractionation procedure used, with 47.0 to 88.3 per cent of the added phosphorus recovered in the

	. Che	eck :	: 40 p	.p.m.
Soil	NH _L F extractable p.p.m.	H ₂ SO _{ll} extractable p.p.m.		H ₂ SO _l extractable p.p.m.
: Altona : 1	і. 143.2 (40.3)	256.0 : (260.0) :	: 76.5	266.0 (269.0)
2	16.9 (11.5)	255.0 : (261.5) :		267.5 (284.0)
3	12.8 (11.5)	355.0 : (354.0) :		375.0 : (388.5) :
<u> </u>	17.2 (14.4)	353.0 : (355.0) :		375.5 : (384.0) :
: Teulon :	2½.7 (21.2)	232.5 (236.0)	.5. 5. 5.	240.0 : (253.0) :
2 2	ીય.8 (36.8)	240.0 (250.0)	75.6	246.0 : (267.5) :
3	23.0 (20.1)	212.0 :: (213.0) ::	: 54.6 :	220.5 : (233.6) :
Winnipeg	35.0 : (31.3)	181.6 (183.0)		: : : : : : : : : : : : : : : : : : :
2	21.0 : (16.7) :	242.0 (250.0)	(33.9) :	257.1 : (274.0) :
; 3 ;	14.7 (10.9)	223.9 (266.5)	33.5 : (27.6) :	243.0 : (254.0) :

The figures between brackets represent the analyses of the soil samples after harvesting the oat \mathtt{crop}_{\bullet}

NH), F extract. The remaining added phosphorus was H_2SO_L extractable.

In both the check and 40 p.p.m. treatments, the NH_LF-extractable phosphorus from the different samples were highly correlated with the phosphorus uptake by the oat plants. The correlation coefficient was +0.927 which was significant at the 1 per cent level. This suggests that the NH_LF-extractable phosphorus is highly related to the phosphate forms available to the plants. It was also found that the NH_LF-extractable phosphorus was highly correlated with the phosphorus amounts extracted by Clsen's NaHCO3-extraction method from the same treatments. The correlation coefficient was +0.913 which was significant at the 1 per cent level. The H₂SO_L-extractable phosphorus was not related to either phosphorus uptake by the oat plants or the NaHCO3-extractable phosphorus.

The analyses at the end of the greenhouse experiment reflect variable decreases in the NH_LF-extractable phosphorus. At the same time comparable increases in the H₂SO_L-extractable phosphorus were observed in all the samples. This suggests that some of the NH_LF-extractable phosphate was converted to a calcium bound form. However, the reductions in NH_LF-extractable phosphorus from the different samples were not related to the CaCO₃ content of these samples. This indicates that the phosphate transformation process was independent of the CaCO₃ content.

It is noted that the total inorganic phosphorus of the samples at the end of the greenhouse experiment was almost equal to amounts before seeding time, which does not account for the amounts removed by the oat plants. This could be attributed to: (a) mineralization of soil organic phosphorus. This suggestion is supported by Van Diest and Elack's conclusion (39) that the phosphorus present in organic form in alkaline soils at the beginning of a season may contribute substantially to the phosphorus nutrition of plants grown during that season; (b) experimental error. This could be a large factor since the amounts of phosphorus removed by the oat plants were fairly small compared to the total inorganic phosphorus content of the different samples.

The particle size distribution of the carbonate materials in the soil samples are reported in Table XIV. It is noted that with the exception of Altona 3 sample, the majority of the carbonate materials as expressed as CaCO₃ were found in the silt fraction. However, the data did not present any specific explanation for the trends observed from the greenhouse data.

Statistical analyses of the presented data shows the existence of a highly significant positive correlation between the amounts of phosphorus taken up by the oat plants and the amounts of phosphorus extracted by two chemical methods from either the check or the phosphorus treated samples. The correlation coefficients for these relationships were 0.892 and 0.913 for the NaHCO3- and the NH_LF- (Jackson procedure) extractable phosphorus respectively. Thus, an investigation of the phosphate forms extractable by both procedures would serve as sound basis for a comprehensive discussion of the role played by the carbonate content of the soil samples in the availability of recently added and

DISTRIBUTION OF CaCO3 AMONG THE SAND, SILT, AND CLAY FRACTIONS EXPRESSED

AS A PERCENTAGE OF THE TOTAL RECOVERED

TABLE XIV

Soil	: : Sand fraction : % :	: : Silt fraction : % :	: : Clay fraction : % :	Total CaCO3 (expressed as a percentage of the soil)
: Altona : 1	6 6	100.0	p p p p p p en ung tim cau	: : : 0.7
2	100.0	A and ESS TOO COM	0 9 0 0 april 1 mark 1 may appi	: : 1.1 :
3	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	16.0	84.0	8.2
: 4	6.5	71.2	22.3	: 12.5 :
Teulon	: 10.1	£47.6	l ₁ 2.3	: 23.8
2	9.8	67.1	3.1	<i>2</i> 9.8
. 3	: 11.3	63.9	24.8	; ; 30.1
<pre>Winnipeg l </pre>	12.5	87.5	o one may live took	3.0
2	: 13.2	80.6	6.2	14.7
3	11.6	69.4	19.0	36.2

native soil phosphate. In the following discussions the carbonate content of the samples will be expressed as CaCO3 equivalent, bearing in mind that other forms of insoluble carbonate could be present in the soil.

The extraction mechanism of the NaHCO₃ reagent, as explained by Olsen (24) and Jackson (19), is based on: (a) lowering the Ca++ activity in the soil solution, as a result of increasing the carbonate ion activity. Thus phosphate is released from the surface of calcium phosphate according to the solubility product principle; (b) the probable competition of HCO₃-, CO₃-, and OH- ions for phosphate adsorbed on the surface of soil particles; (c) the ability of the reagent to extract some phosphate from the surface of aluminum and iron phosphates by repressing the aluminum and iron ions activities by formation of an aluminate complex of the former and precipitating the latter as the oxide.

Olsen (23) found that NaHCO3-extractable phosphorus from 25 soils, with pH ranging from 5.0 to 7.6, was highly correlated with surface phosphate in these samples. The latter was determined by P32 equilibrium technique. The correlation coefficient was 0.938 which was significant at the 1 per cent level. Seven of the samples contained CaCO3. Patel and Mehta (28) fractionated the total phosphorus of 21 soils, with CaCO3 content ranging from nil to 6.6, into five components viz. (a) calcium phosphate, (b) adsorbed phosphate (c) iron and aluminum phosphate (d) organic phosphate (e) insoluble phosphate. They found that the amounts of adsorbed phosphate gave the highest

correlation with the uptake of phosphorus by sorghum plants (r=+0.836). Meanwhile the adsorbed phosphate was highly correlated with the NaHCO₃-extractable phosphorus (r=+0.933).

The previous discussion provides ample evidence that the amount of NaHCO3-extractable phosphorus is highly related to surface phosphate in the soil.

There is considerable evidence which indicates that MHLFextractable phosphorus is highly related to surface phosphate in the soil. In the modified Chang and Jackson's procedure the NHAF reagent is considered to extract loosely bound and aluminum phosphates in the soil. Turner and Rice (36) attributed the efficiency of the NH_LF reagent in liberating phosphorus adsorbed by aluminum hydroxide to the formation of an insoluble (NH) 3AlF6 complex on the gel surface. This could be the same mechanism with which the NH, I solution extracts the phosphorus adsorbed by clay minerals. This suggestion is supported by Gorbunov's conclusion (16) that phosphorus adsorbed by clay minerals is related to the active surface aluminum of the clay crystals. Bray and Dickman (3) considered that NH,F solutions extracted water soluble and easily replaceable phosphate from soils and clay. Weir and Soper (42), in their adsorption and exchange studies in some Manitoba soils, concluded that a high percentage of the NHLF-extractable phosphorus was exchangeable with P32. It was also found in the writer's investigation that the NH, F-extractable soil phosphorus from the check samples was highly correlated with the soil phosphate exchangeable with P32 which was determined according to Sokolov's method (r=+0.801). Since

exchangeability with P32 is characteristic of surface phosphate, it could be concluded that NH_LF-extractable phosphorus is highly related to surface phosphate in the soil. The capability of calcareous soils to adsorb considerable amounts of phosphorus on the surface of the soil particles has been demonstrated by many investigators, including Weir and Soper (42) and Olsen and Watanabe (25). They found that phosphorus adsorption by calcareous soils follows the Langmuir isotherm within low ranges of initial phosphorus concentration in solution. In general, these concentrations would include the normal rate of phosphorus fertilizer applications to soils. It also includes the rates of phosphorus application in the present investigation.

The previous discussion indicates that both NaHCO3- and NH_{l_1}F-extractable phosphorus are closely related to phosphorus held on the surface of the soil particles. Since NaHCO3- and NH_{l_1}F-extractable phosphorus are also highly correlated with phosphorus uptake by the oat plants, it is justified to assume that the phosphorus available to the oat plants is highly related with the phosphorus held on the surface of the soil particles. Olsen (23) reported similar relationships between the surface phosphorus of 25 calcareous soils and available soil phosphorus estimated by "A" values. Cole and Olsen (7, 8) studied phosphorus solubility in some calcareous soils through the determination of the mean activity of dicalcium phosphate (a Ca++ x a HPO $_{l_1}$) in equilibrated soil solutions. They found that phosphorus solubility increases regularly with the amounts of phosphorus adsorbed in the monolayer region on surfaces of various materials likely to be

present in calcareous soils. They concluded that the differences in phosphorus solubility behaviour among calcareous soils of varying texture is related to both the capacity of these soils for monolayer adsorption of phosphorus and the percentage phosphorus saturation of the soil surface area. Olsen and Watanabe (25) found that the adsorption maximum of ten calcareous soils as calculated from the Langmuir isotherm was closely correlated with the surface area of these soils measured by ethylene glycol retention. Chang and Chu (4) suggested that soluble phosphates added to a given soil is initially held in soluble forms by aluminum, iron, and calcium cations on the surface of the solid phases with which the phosphate comes in contact.

Since the CaCO₃ of a given calcareous soil forms an integral part of the total surface area of this soil, thus an investigation of the reactivity of CaCO₃ surface would throw considerable light on its role in the availability of recently added and native soil phosphate. Boischot et al. (2) showed that considerable amounts of phosphorus could be adsorbed on the surface of CaCO₃ in a form easily desorbed. This was confirmed by Cole et al. (9) who found that within a low range of added phosphate concentrations, phosphorus is adsorbed in a monolayer on the surface of CaCO₃ in close agreement to the Langmuir isotherm. They also found that nearly all the adsorbed phosphorus was readily exchangeable with P32 in solution. Cole and Olsen (8) found that other soil components such as clay minerals, which are highly base saturated in calcareous soils, adsorb phosphorus in a behaviour similar to that of CaCO₃. It is thus apparent that the CaCO₃

surface forms only a part of the adsorption complex in calcareous soils. Since the total surface area or the adsorption capacity of a soil is not dependent on the relative amount of a single component such as CaCO₃, this would help to explain the lack of correlation between the availability of added phosphorus and the CaCO₃ content of the soil found in this investigation. Cole and Olsen (8) also concluded that detailed information about the kind of surface present (clay minerals, CaCO₃, etc.) was not needed to describe the effects of soil texture on phosphorus solubility in calcareous soils.

It is apparent from the previous discussion that the surface area of a given soil has an important influence on the soil supplying power. Since the surface area of a soil, in general, is positively related to its colloids content, this would explain the positive correlations found between available soil phosphorus estimated by different methods in the present investigation and the clay and organic matter contents of the soil samples. The role of organic matter as a source of phosphorus could also be taken into consideration.

The analyses after harvesting the oat crop show an appreciable reduction in NaHCO3- and NH_LF-extractable phosphorus. Since phosphorus extracted by both reagents was shown to be highly related to surface phosphate in the soil, the observed reduction could be attributed to reduction in surface phosphate of the samples. This is in agreement with Olsen (23) who presented experimental evidence indicating that the residual phosphate in calcareous soils is present largely as surface phosphate which gradually decreases with time. Cole et al. (9)

noted that the phosphorus adsorbed in a monolayer on the surface of CaCO3 exchanges with P32 progressively less readily the longer the initial sorption period. This was attributed to a gradual penetration of the phosphate ion into cracks and crevices inaccessible to the solutions or to solid diffusion of the ions into the crystal lattice. The reduction in available phosphorus could also be attributed to phosphorus precipitation in a form less available to the plants. However, in the present investigation the reduction in available phosphorus, as indicated by the NaHCO3 and NHLF extractions, was not related to CaCO3 content of the samples.

Nevertheless, the analyses of the soils after harvesting the oat crop also indicate that considerable amounts of the added phosphorus, especially in the 40 p.p.m. treatment, were still available. This suggests that the effect of the added phosphorus would not be confined to one crop. This suggestion is supported by a number of investigations including that of Chumachenko (6) who concluded that soluble phosphorus added to calcareous soils was available for long periods of time.

Clsen et al. (26) found that the efficiency of residual phosphorus in some calcareous soils ranged from 30-50 per cent of the efficiency of freshly added phosphate depending on soil type, texture, and forms of phosphate previously added. Thus it is apparent that the previous management of a given soil is an important factor in its phosphorus supplying power. In the present investigation, the fact that all the data indicated relatively high soil phosphorus availability in Teulon samples could be attributed to past management practices, since these

samples were collected from a field which had received several phosphate applications within the last twenty years*. The Winnipeg soil had not been previously fertilized* while the history of the Altona field is not known.

It is thus clear from the data presented in this investigation, supported by the previous discussions, that the CaCO3 content of a given soil per se could not serve as an indicator of the phosphorus supplying power of this soil. It also could be concluded that the phosphorus status of a given soil is a reaction product of the effects of a number of factors which could include soil type, texture, organic matter content, and previous management.

 $^{^*}$ According to information from the farmer who owned the field.

- 2. A number of factors, including soil texture and previous management, were shown to have an important influence on the availability of soil phosphate.
- 3. There was no evidence of any relationship between the availability of phosphorus, either added in a band or mixed throughout the soil and incubated for a month prior to seeding time, and the carbonate content of the samples.
- 4. Most of the added phosphorus seems to be held initially on the surface of the soil particles in a form or forms available to the plants. These forms are transformed gradually to forms less available or unavailable to the plants. This transformation did not have an apparent relationship with the carbonate content of the samples.
- 5. Highly significant positive correlations were obtained between phosphorus extracted by either NaHCO3 or NH_LF reagents and the uptake of phosphorus by plants.

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